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Tridentate Chelate Compounds. V.[1] Coordination Compounds Derived from Cobalt Salts and 1,3-Disubstituted 1,2-Diaza-2-propenes

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The coordination with cobalt salts of a series of eleven ligands, the last ten of which are derivatives of the first, 1,3-bis(2′-pyridyl)1,2-diaza-2-propene (PAPHY), has been studied. It is shown that incorporation into the PAPHY molecule of substituent groups, which can function as "blocking groups," adjacent to the lateral nitrogen donor atoms of the donor atom sequence can hinder oxidation of the complexed cobalt atom from the cobalt(II) to the cobalt(III) state. Two such blocking groups apparently make impossible the existence of a cobalt(III) complex. This behavior can be accounted for sterically. The magnetic properties of the neutral cobalt(II) complexes studied appear to be anomalous and are discussed.

The ability of diazapropenes of such types as 1,3-bis-(2′-pyridyl)1,2-diaza-2-propene (PAPHY[4]) to coordinate with transition metal salts to give complex salts whose complex cations can be deprotonated was first observed in an experiment involving a cobalt(II) salt.[5] Subsequent studies of the coordination of PAPHY-type ligands with cobalt salts have proved difficult to interpret. This paper describes experiments with eleven different ligands of the PAPHY-type. Certain of their structural features appear to be important for an understanding of their coordination behavior. Hence, their formulas are set out in full (Fig. 1).

With the single exception of VI each of these ligands can be readily seen to be a derivative of I. Each has been modified by incorporation into its molecules of substitutent methyl groups or of benzene ring systems fused with one or the other or both of the pyridine rings of I. The ligands fall naturally into the three groups: (a) I, II, and III, in the molecules of each of which the methine carbon atom of each of the pyridine rings adjacent to the ring nitrogen atom but other than the point of attachment of this ring to the diazapropene chain is unsubstituted; (b) IV, V, VII, and VIII, in the molecules of which one only of these methine carbon atoms is substituted by a "blocking group" (methyl or the methine corner of a fused benzene ring); and (c) IX, X, and XI, in which the adjacent methine corners of *both* of these pyridine rings are substituted by blocking groups.

The ligand VI differs a little from the others in that when coordinated to a metal the "chelate loops" formed are five-membered and six-membered instead of both being five-membered as in the complexes of I. Spatially, this brings the 2-carbon atom of the quinoline nucleus into such a position during coordination that it might almost be considered as a blocking group by itself. VI may, therefore, be considered as belonging to group b.

Ligands of the first group (I, II, and III) react with cobalt(II) perchlorate in aqueous ethanol solution to give cobalt(III) complex salts of the formula $[Co(lig)(H\text{-}lig)](ClO_4)_2$[6] (Table II). As noted by Lions and Martin[5] for PAPHY (I) a solution of each ligand acts as an oxidizing agent toward the cobalt(II) salt. The cations of the complex salt obtained each contain two ligand residues of which one has lost a proton. The salts are diamagnetic and are clearly cobalt(III) complexes.

Recrystallization of these three singly deprotonated compounds from aqueous ethanol leads to deprotonation of the second ligand residue in each cation and formation of salts of the formula $[Co(lig)_2](ClO_4)$ (Table III).

With the exception of ligand IX (which is very insoluble and intractable) all the other ligands from groups b and c (IV, V, VI, VII, VIII, X, and XI) react readily in aqueous ethanol with cobalt(II) perchlorate to give complex cobalt(II) compounds of the formula $[Co(H\text{-}lig)_2](ClO_4)_2$ (Table IV).

Treatment with sodium hydroxide of solutions of such compounds from the ligands IV, V, and VI produces red or red-violet solutions. The substances responsible for the colors can be extracted into chloroform and recovered after drying and evaporation of the solvent chloroform as dichroic red-green solids of variable composition. Analyses suggest that each such product is a mixture of two compounds, $[Co(lig)_2]$ and $[Co(lig)_2](ClO_4)$. The magnetic moments (1.5–2.0 B.M.) indicate the presence of relatively large amounts of the cobalt(III) complex salt.

Extraction with benzene of solutions of the complex salts of the type $[Co(H\text{-}lig)_2](ClO_4)_2$ prepared from each of the ligands IV, VIII, and XI and then made alkaline with sodium hydroxide leads to isolation of the deprotonated cobalt(II) complexes $[Co(lig)_2]\cdot 2H_2O$ (Table V) in good yield. Similar extraction of the corresponding alkaline solution prepared from $[Co(H\text{-}lig\text{-}V)_2](ClO_4)_2$ gives only a small yield of $[Co(lig\text{-}V)_2]\cdot H_2O$, while none of the corresponding $[Co(lig\text{-}VII)_2]$

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[1] For the previous paper in this series, see B. Chiswell, F. Lions, and M. L. Tomlinson, *Inorg. Chem.*, **3**, 492 (1964).

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[4] J. F. Geldard and F. Lions, *Inorg. Chem.*, **2**, 270 (1963).

[5] F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **80**, 3861 (1958).

[6] Any one of the ligands I–XI can be referred to as H-lig. If a specific ligand is referred to its number is added. Thus, PAPHY is H-Lig-I. If such a ligand residue is coordinated with a metal ion and then deprotonated the H is omitted.

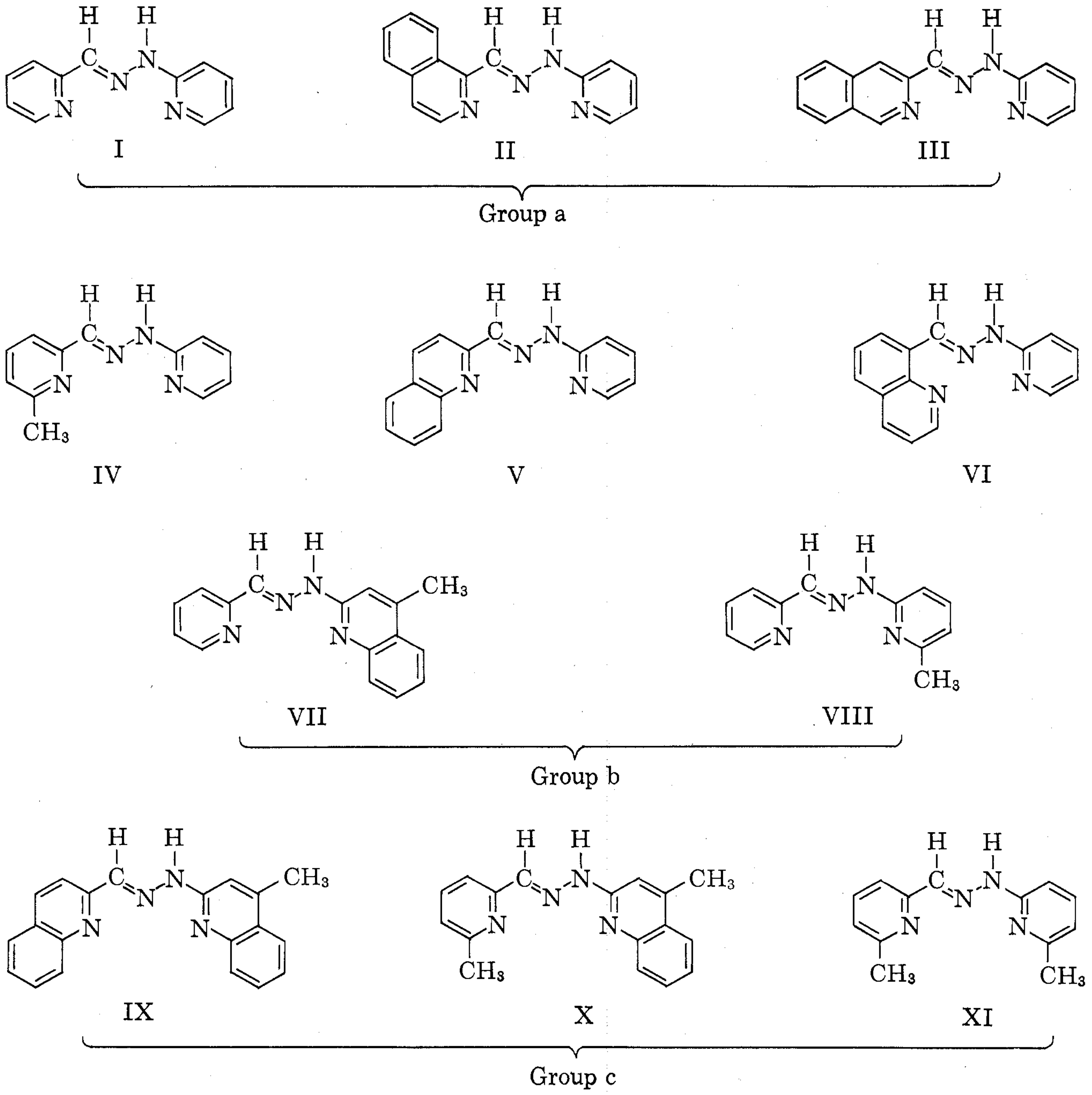

Figure 1.

can be obtained in this way. It should be pointed out here that the magnetic moments of these deprotonated complexes are abnormal (Table VI). This causes difficulties of interpretation and is discussed later.

If, after benzene extraction of the alkaline solutions obtained from $[Co(H\text{-}lig)_2](ClO_4)_2$ salts prepared from the ligands IV, V, VII, and VIII, these alkaline solutions are further extracted with chloroform, it is possible to remove and to isolate the doubly deprotonated cobalt(III) complex salt $[Co(lig)_2](ClO_4)$ (Table III). Ligands V and VII gave cobalt(III) complex salts of this type in good yield. However, the compounds $[Co(lig\text{-}X)_2](ClO_4)$ and $[Co(lig\text{-}XI)_2](ClO_4)$ cannot be prepared in this way. It is worth commenting here that these results are readily reproducible and the properties of the products obtained, especially the unusual magnetic moments, are the same for different preparations of the same compound.

Ligands of group b which can be converted (IV and VII readily, V in poor yield) as above to doubly-deprotonated neutral cobalt(II) complexes react with cobalt(II) perchlorate in aqueous ethanol in the presence of hydrogen peroxide to give the doubly-deprotonated cobalt(III) salts $[Co(lig)_2](ClO_4)$. Cobalt(II) complexes cannot be isolated when peroxide is used. Further, even from solutions containing excess perchloric acid salts of the type $[Co(lig)(H\text{-}lig)](ClO_4)_2$ could not be isolated.

TABLE I

LIGANDS (1,3-DISUBSTITUTED 1,2-DIAZA-2-PROPENES, R′NHN=CHR″)[a]

No.	R′	R″	Formula	M.p., °C.	Calcd., % C	Calcd., % H	Found, % C	Found, % H
VII	4-Methyl-2-quinolyl	2-Pyridyl	$C_{16}H_{14}N_4$	197–199	73.3	5.4	73.4	5.7
VIII	6-Methyl-2-pyridyl	2-Pyridyl	$C_{12}H_{12}N_4$	147–148	67.9	5.7	67.9	5.2[b]
IX	4-Methyl-2-quinolyl	2-Quinolyl	$C_{20}H_{16}N_4$	242–243	76.9	5.2	77.2	5.3
X	4-Methyl-2-quinolyl	6-Methyl-2-pyridyl	$C_{17}H_{16}N_4$	200–203	73.9	5.8	74.0	5.9
XI	6-Methyl-2-pyridyl	6-Methyl-2-pyridyl	$C_{13}H_{14}N_4$	207–208	69.0	6.2	68.8	6.1[c]

[a] Ligands I–VI have already been described (ref. 4 and 5). [b] Calcd.: N, 26.4. Found: N, 25.8. [c] Calcd.: N, 24.8. Found: N, 24.5.

TABLE II

COBALT(III) SALTS OF FORMULA $[Co(lig)(H\text{-}lig)](ClO_4)_2$

Compd. no.	Ligand	Formula[a]	Calcd., % C	Calcd., % H	Calcd., % N	Calcd., % Co	Calcd., % Cl	Found, % C	Found, % H	Found, % N	Found, % Co	Found, % Cl	Molar conductivity, ohm^{-1} cm.^{2} Water	Molar conductivity, ohm^{-1} cm.^{2} Nitrobenzene
XII	I	$[CoC_{22}H_{19}N_8](ClO_4)_2$											462	52.1
XIII	II	$[CoC_{30}H_{23}N_8](ClO_4)_2$	47.7	3.4	14.9	7.8	9.5	47.6	3.6	13.8	7.5	9.6	453	48.3
XIV	III	$[CoC_{30}H_{23}N_8](ClO_4)_2$	47.7	3.4	14.9	7.8	9.5	47.7	3.8	14.1	7.6	9.5	482	40.2

[a] Compound XII has already been described (see text). The names of the other compounds are: XIII, (1-(2′-pyridyl)-3-(1″-isoquinolyl)1,2-diaza-2-propenato)(1-(2′-pyridyl)3-(1″-isoquinolyl)1,2-diaza-2-propene)cobalt(III) perchlorate; XIV, (1-(2′-pyridyl)3-(3″-isoquinolyl)1,2-diaza-2-propenato)(1-(2′-pyridyl)3-(3″-isoquinolyl)1,2-diaza-2-propene)cobalt(III) perchlorate. Both were prepared by method A.

On the other hand, ligands of group c (X and XI) react in aqueous ethanol solution with cobalt(II) perchlorate even in the presence of peroxide to give $[Co(H\text{-}lig)_2](ClO_4)_2$-type compounds. Neither these compounds nor the corresponding deprotonated cobalt(II) neutral complexes derived from them with alkali can be oxidized to the corresponding cobalt(III) compounds. It was also observed that interaction of either ligand X or ligand XI with sodium tris(carbonato)cobaltate(III)[7] in perchloric acid solution led to formation of the corresponding cobalt(II) complex salt $[Co(H\text{-}lig)_2](ClO_4)_2$. Apparently no cobalt(III) complex was produced from either ligand, the cobalt in these experiments being reduced from cobalt(III) to cobalt(II).

Experimental

As far as possible the results obtained experimentally are tabulated. Starting materials were either purchased and purified or synthesized by known methods.

Ligands.—Each of the ligands I–XI (Table I) was prepared by heating together in fairly concentrated ethanolic solution (5 min. on the steam bath) stoichiometric proportions of the hydrazine and the aldehyde. The solution was then carefully diluted with water and cooled. The product crystallized in yellow needles. Each ligand was recrystallized from aqueous ethanol with the exception of IX which was recrystallized from ethyl acetate or aqueous dimethylformamide. 4-Methylquinolyl-2-hydrazine was prepared from 4-methyl-2-hydroxyquinoline by the method of Perkin and Robinson[8]; 6-methylpyridyl-2-hydrazine was prepared from the 6-methyl-2-bromopyridine of Case and Kasper.[9]

Complexes.—Various methods of preparation were used as follows.

(A) An aqueous solution of cobalt(II) perchlorate (one molecular proportion) was mixed with an ethanolic solution of the ligand (two molecular proportions). Compounds XII, XIII, and XIV (Table II) prepared by this method were not recrystallized.

(B) The compounds XII, XIII, and XIV were recrystallized from aqueous ethanol to give the corresponding doubly-deprotonated complexes.

(C) Sodium hydroxide solution was added to an aqueous ethanolic solution of the complex perchlorate $[Co(H\text{-}lig)_2](ClO_4)_2$. An intense red-brown color developed immediately. The solution was extracted twice with benzene, and the combined benzene extracts were washed twice with a little water and dried with anhydrous sodium sulfate. Concentration of the benzene solution and addition of petroleum ether led to precipitation of the product. Usually, it was recrystallized from aqueous ethanol.

(D) An aqueous solution of cobalt(II) perchlorate (one molecular proportion) was added to a hot solution of the ligand IX (two molecular proportions) in hot N-methylpyrrolidone. After filtration and then dilution with more water the product (**XXXIV**) crystallized as a very sparingly soluble purple-blue powder.

(E) This method was exactly similar to (C) except that chloroform was used for the extractions instead of benzene.

(F) The aqueous solution remaining after benzene extraction described in (C), if highly colored, was extracted further with chloroform and the extracted solid recovered from the chloroform extracts by evaporation. It was then recrystallized from aqueous ethanol.

(G) Hydrogen peroxide solution was added to an aqueous ethanolic solution of the complex salt $[Co(H\text{-}lig)_2](ClO_4)_2$. The solution was then heated on a steam bath for approximately 30 min. The product was isolated either by evaporation and then crystallization or, alternatively, by extraction into chloroform and recovery. No cobalt complex could be extracted into benzene from any of the reaction solutions.

Magnetic Moments.—The magnetic moments of most of the complexes prepared were measured in air at room temperature (20–22°) using a Gouy balance and are set out in Table VI.

Conductivities.—Conductivities were determined using a Philips Philoscope with platinum electrodes of the dip type at room temperature (20–22°). The nitrobenzene used was pure and dry.

Discussion

Experiment shows that a solution of PAPHY behaves toward cobalt(II) salts as an oxidizing agent as well as a chelating agent. Coordination is accompanied immediately by loss of an electron from the coordinated cobalt(II) ion and simultaneous deprotonation of one of the tridentate residues. The resultant

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[7] *Cf.* H. F. Bauer and W. C. Drinkard, *J. Am. Chem. Soc.*, **82**, 5031 (1960).

[8] W. H. Perkin, Jr., and R. Robinson, *J. Chem. Soc.*, **103**, 1978 (1913).

[9] F. H. Case and T. J. Kasper, *J. Am. Chem. Soc.*, **78**, 5842 (1956).

TABLE III

COBALT(III) SALTS OF THE FORMULA $[Co(lig)_2]ClO_4 \cdot nH_2O$

Compd. No.	Ligand	Formula[a]	Calcd., %					Found, %					Molar conductivity, ohm^{-1} cm.^{2}
			C	H	N	Co	Cl	C	H	N	Co	Cl	Nitrobenzene
XV	I	$[CoC_{22}H_{18}N_8]ClO_4 \cdot 0.5H_2O$	47.0	3.4	20.0	10.5	6.3	47.1	3.3	19.5	10.5	6.5	24.3
XVI	II	$[CoC_{30}H_{22}N_8]ClO_4 \cdot 2H_2O$	52.2	4.0	16.2	8.5	5.1	52.2	3.8	15.6	8.3	5.5	25.2
XVII	III	$[CoC_{30}H_{22}N_8]ClO_4 \cdot H_2O$	53.6	3.8	16.7	8.8	5.3	53.7	3.7	16.1	8.7	5.1	23.6
XVIII	IV	$[CoC_{24}H_{22}N_8]ClO_4 \cdot 1.5H_2O$	47.3	4.1	18.4	9.7		47.0	4.0	17.8	9.8		21.3
XIX	V	$[CoC_{30}H_{22}N_8]ClO_4$	55.2	3.4	17.2	9.0		55.3	3.9	16.4	9.0		23.8
XX	VII	$[CoC_{32}H_{26}N_8]ClO_4$	56.4	3.9		8.7		56.4	4.4		8.3		27.8
XXI	VIII	$[CoC_{24}H_{22}N_8]ClO_4 \cdot H_2O$	48.1	4.0	18.7	9.8		48.2	4.1	18.0	9.7		25.4

[a] Names of compounds: XV, bis(1,3-di(2′-pyridyl)1,2-diaza-2-propenato)cobalt(III) perchlorate–0.5-water; XVI, bis(1-(2′-pyridyl)3-(1″-isoquinolyl)1,2-diaza-2-propenato)cobalt(III) perchlorate–2-water; XVII, bis(1-(2′-pyridyl)3-(3″-isoquinolyl)1,2-diaza-2-propenato)cobalt(III) perchlorate–1-water; XVIII, bis(1-(2′-pyridyl)3-(6″-methyl-2″-pyridyl)1,2-diaza-2-propenato)cobalt(III) perchlorate–1.5-water; XIX, bis(1-(2′-pyridyl)3-(2″-quinolyl)1,2-diaza-2-propenato)cobalt(III) perchlorate; XX, bis(1-(4′-methyl)-2′-quinolyl)3-(2″-diaza-2-propenato)cobalt(III) perchlorate; XXI, bis(1-(6′-methyl-2′-pyridyl)3-(2″-pyridyl)1,2-diaza-2-propenato)cobalt(III) perchlorate–1-water.

TABLE IV

COBALT(II) SALTS OF THE FORMULA $[Co(H\text{-}lig)_2](ClO_4)_2 \cdot nH_2O$

Compd. no.	Ligand	Formula[a]	Calcd., %				Found, %				Molar conductivity, ohm^{-1} cm.^{2}	
			C	H	N	Co	C	H	N	Co	Water	Nitrobenzene
XXII	IV	$[CoC_{24}H_{24}N_8](ClO_4)_2 \cdot 2H_2O$	40.2	3.9	15.6	8.2	40.3	4.0	14.9	8.2	474	56.4
XXIII	V	$[CoC_{30}H_{24}N_8](ClO_4)_2$	47.8	3.2	14.9	7.8	47.5	3.6	14.3	7.8	374	45.9
XXIV	VI	$[CoC_{30}H_{24}N_8](ClO_4)$	47.8	3.2	14.9	7.8	47.7	3.6	14.4	7.8	482	40.2
XXV	VII	$[CoC_{32}H_{28}N_8](ClO_4)_2 \cdot 2H_2O$	46.9	3.9	13.7	7.2	47.3	3.9	13.5	7.7		51.0
XXVI	VIII	$[CoC_{24}H_{24}N_8](ClO_4)_2 \cdot H_2O$	41.1	3.7	16.0	8.4	41.2	4.1	14.9	8.2		54.4
XXVII	X	$[CoC_{34}H_{22}N_8](ClO_4)_2 \cdot 3H_2O$	47.2	4.4		6.8	46.9	4.7		6.6		38.2
XXVIII	XI	$[CoC_{26}H_{28}N_8](ClO_4)_2$	43.9	3.9	15.8	8.3	43.8	4.1	15.0	8.2		53.7

[a] Names of compounds (colors in parentheses): XXII, bis(1-(2′-pyridyl)3-(6″-methyl-2″-pyridyl)1,2-diaza-2-propene)cobalt(II) perchlorate–2-water (fawn); XXIII, bis(1-(2′-pyridyl)3-(2″-quinolyl)1,2-diaza-2-propene)cobalt(II) perchlorate (red-brown); XXIV, bis(1-(2′-pyridyl)3-(8″-quinolyl)1,2-diaza-2-propene)cobalt(II) perchlorate (red-brown); XXV, bis(1-(4′-methyl-2′-quinolyl)3-(2″-pyridyl)1,2-diaza-2-propene)cobalt(II) perchlorate–2-water (brown); XXVI, bis(1-(6′-methyl-2′-pyridyl)3-(2″-pyridyl)1,2-diaza-2-propene)cobalt(II) perchlorate–1-water (dark brown); XXVII, bis(1-(4′-methyl-2′-quinolyl)3-(6″-methyl-2″-pyridyl)1,2-diaza-2-propene)cobalt(II) perchlorate–3-water (brown); XXVIII, bis(1,3-di(6′-methyl-2′-pyridyl)1,2-diaza-2-propene)cobalt(II) perchlorate (brown).

TABLE V

NEUTRAL COBALT(II) COMPLEXES OF THE FORMULA $[Co(lig)_2] \cdot nH_2O$

Compd. no.	Ligand	Formula[a]	Method	Calcd., %				Found, %			
				C	H	N	Co	C	H	N	Co
XXIX	IV	$[CoC_{24}H_{22}N_8] \cdot 1.5H_2O$	C	56.8	4.9	22.1	11.6	56.6	4.9	21.9	12.0
XXX	V	$[CoC_{30}H_{22}N_8] \cdot H_2O$	C	63.0	4.2	19.6	10.3	63.3	4.3	19.7	10.6
XXXI	VIII	$[CoC_{24}H_{22}N_8] \cdot H_2O$	C	57.7	4.4	22.4	11.8	57.7	4.6	22.0	11.8
XXXII	IX	$[CoC_{40}H_{30}N_8] \cdot H_2O$	D	68.6	4.6		8.4	68.9	4.6		8.5
XXXIII	X	$[CoC_{34}H_{30}N_8]$	E	67.1	4.9		9.7	67.0	5.2		9.3
XXXIV	XI	$[CoC_{26}H_{24}N_8]$	C + E	59.3	5.0	21.3	11.2	59.2	5.2	20.3	10.9

[a] Names of compounds: XXIX, bis(1-(2′-pyridyl)3-(6″-methyl-2″-pyridyl)1,2-diaza-2-propenato)cobalt(II)–1.5-water; XXX, bis(1-(2′-pyridyl)3-(2″-quinolyl)1,2-diaza-2-propenato)cobalt(II)–1-water; XXXI, bis(1-(6′-methyl-2′-pyridyl)3-(2″-pyridyl)1,2-diaza-2-propenato)cobalt(II)–1-water; XXXII, bis(1-(4′-methyl-2′-quinolyl)3-(2″-quinolyl)1,2-diaza-2-propenato)cobalt(II)–1-water; XXXIII, bis(1-(4′-methyl-2′-quinolyl)3-(6″-methyl-2″-pyridyl)1,2-diaza-2-propenato)cobalt(II); XXXIV, bis(1,3-di(6′-methyl-2′-pyridyl)1,2-diaza-2-propenato)cobalt(II). Compound XXXII was deep bluish purple in color. The other five complexes were dichroic red-green. All had negligible conductivity in nitrobenzene solution.

salt is diamagnetic (Table VI). Further deprotonation of the second ligand residue in the complex cation is very easily accomplished and a uni-univalent diamagnetic salt is obtained. It might well be expected that derivatives of PAPHY containing the essential $-\mathrm{N{=}}\overset{|}{\mathrm{C}}\mathrm{{-}NH{-}N{=}}\overset{|}{\mathrm{C}}{-}\overset{|}{\mathrm{C}}\mathrm{{=}N}$ sequence of donors (capable by deprotonation of conversion to the $=\mathrm{N}-\overset{|}{\mathrm{C}}\mathrm{{=}N{-}N{=}}\overset{|}{\mathrm{C}}{-}\overset{|}{\mathrm{C}}\mathrm{{=}N}-$ sequence) would behave similarly. This expectation is realized with ligands of group a.

If a substituent "blocking" group (methyl, or the methine corner of a fused benzene ring) is built into the PAPHY molecule adjacent to one or the other of the pyridine ring donor nitrogen atoms, the spontaneous oxidizing power of the ligand toward the cobalt(II) ions with which it becomes coordinated is markedly reduced, although it is still possible to effect oxidation of cobalt to cobalt(III) in the complexes obtained. Oxidation appears to occur most easily during deprotonation with alkalies. However, it is particularly noticeable that this oxidation is more difficult when the "blocking group" is methyl rather than the methine corner of a fused benzene ring. Similar space effects are found in the biphenyl series.

When two blocking groups are built into the ligand molecule oxidation to the cobalt(III) state appears to become impossible. Indeed, if a cobalt(III) compound, such as sodium tris(carbonato)cobaltate (III), is caused to interact with such a ligand, the high chelating power of the PAPHY-type ligand is exerted so that two ligand residues coordinate but the cobalt is *reduced* to the cobalt(II) state. Thus, the oxidation state of the metal ion in these coordination complexes would appear to be controlled by the structural make-up of the ligand.

Models show quite clearly that when blocking groups are incorporated into the PAPHY molecule (as in the substances IV–XI) it becomes much more difficult for two such molecules to act as planar tridentate chelate groups attached to a single six-coordinate metal atom with six donor nitrogen atoms octahedrally disposed. The difficulty is increased by *diminution* of the metal atom size.

There is considerable difficulty in estimating the degree of contraction undergone by a six-coordinate cobalt atom when its oxidation state is changed from cobalt(II) to cobalt(III). Thus, Stranks[10] quotes the bond lengths in the hexaamminecobalt(II) and hexaamminecobalt(III) ions as Co^{II}–N, 2.5 Å., and Co^{III}–N, 2.05 Å. Pauling[11] quotes the radius of the octahedral cobalt(II) atom as 1.32 Å. and that of the cobalt(III) atom as 1.22 Å. This is a much smaller difference but it is still considerable.

Whatever the magnitude of the contraction, it would seem that loss of an electron from the cobalt atom during oxidation must be accompanied by some contraction. Tridentate diazapropenes of the type used in this work form extraordinarily stable metal complexes,[12] so that any steric difficulties involved in the contraction of a complex because of alteration of the oxidation state of the complexed metal cannot be resolved by disengagement of one or the other of the tridentate ligand residues. The easiest solution to the problem posed to the complex molecule is retention of the electron by the metal atom and prevention of the contraction. It is obvious that further work must be carried out and confirmation of these ideas sought by studies of the coordination of ligands such as XI with other transition metals capable of exhibiting different oxidation states.

Changes in the electronegativities of the lateral donor nitrogen atoms of the tridentate sequence are considered to be of minor importance in the determination of the oxidation state of the complexed cobalt. Thus, for example, all four members of the two pairs of ligands II and III and V and VI are isomers and differ only in the position of attachment of a fused benzene ring to the PAPHY molecule. The former pair of ligands yields cobalt(III) complexes, the latter pair only cobalt(II) compounds when caused to react with cobalt(II) perchlorate in neutral solution.

Magnetic Moments.—Especially worthy of comment are the low moments of the complexes formulated as $[Co(lig)_2]\cdot H_2O$. It could be reasoned that these are mixtures containing some cobalt(II) complex and some cobalt(III) complex. If this were true the zero conductivities indicate that the cobalt(III) species present must be nonionic. Compounds XXIX, XXX, XXXI, and XXXII are formulated (as the result of analysis) as hydrated cobalt(II) complexes. It would be possible to postulate detachment from a coordination position in the coordination octahedron of the pyridine ring nitrogen donor atom derived originally from the pyridine-2-aldehyde precursor of the ligand and occupation of the vacant coordination position by a water molecule. Deprotonation of this could then give a cobalt(III) nonconducting neutral complex formulated $[Co(lig)_2OH]$. This would be practically impossible to distinguish from the cobalt(III) complex $[Co(lig)_2]\cdot H_2O$ analytically.

TABLE VI

MAGNETIC MOMENTS (IN BOHR MAGNETONS) OF COBALT COMPLEXES[a]

Ligand	$[Co(H\text{-}lig)_2](ClO_4)_2\cdot nH_2O$ (Table IV)		$[Co(lig)_2]\cdot nH_2O$ (Table V)	
IV	XXII	4.9	XXIX	3.1, 3.0
V	XXIII	4.4	XXX	3.7, 3.65
VI	XXIV	3.4		
VII	XXV	4.4		
VIII	XXVI	4.8	XXXI	3.1
IX			XXXII	3.3
X	XXVII	4.8	XXXIII	3.6
XI	XXXVIII	4.9	XXXIV	3.2

[a] Compounds XII–XIV, $[Co(lig)(H\text{-}lig)](ClO_4)_2$ (Table II), and XV–XXI, $[Co(lig)_2](ClO_4)\cdot nH_2O$ (Table III), have zero moment.

There are powerful objections to such a formulation. Detachment of the pyridine aldehyde ring nitrogen atom of one ligand residue from a coordination position might well be considered possible for ligands IV and V (compounds XXIX and XXX). However, it is difficult to understand similar behavior for a ligand such as VIII (compound XXXI) in which the blocking group would be maintained in position. We have accumulated sufficient evidence to date to be strongly of the opinion that deprotonation of a coordinated 2-pyridylhydrazone residue can only occur when the pyridine nitrogen atom and the distal nitrogen atom of the hydrazine residue are simultaneously bonded to metal.

A further objection is that formulation of the substances listed in Table V as mixtures is opposed by the reproducibility of the magnetic moments. Variable results would be expected with mixtures.

Finally, it should be noted that compounds XXXIII

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[10] D. R. Stranks, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 151.

[11] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 249.

[12] R. W. Green, P. S. Hallman, and F. Lions, *Inorg. Chem.*, **3**, 376 (1964).

TABLE VII

VISIBLE–ULTRAVIOLET ABSORPTION SPECTRA (IN ETHANOL)

Ligand	Compd. no.	Maxima	
		λ, mμ	$\epsilon \times 10^{-4}$
I	XV	305	16.6
		455	17.9
III	XVII	312	7.81
		362	6.08
		522	4.74
IV	XXII	296	5.75
		360	7.08
		485	3.86
IV	XXIX	304	6.21
		~355 (sh)	...
		485	7.21
V	XXIII	287	5.23
		321	4.34
		405	1.76
		495	3.64
V	XXX	287	8.08
		322	6.93
		405	3.12
		495	6.07

and XXXIV are not hydrates, yet still exhibit magnetic moments of the same order as the other compounds listed in Table V. The conclusion must then be reached that the magnetic moments for cobalt in these compounds are anomalous. It has already been reported[13] that complex cobalt(II) salts containing two 2,6-bis(2′-pyridyl)pyridine (terpyridine) residues of the type $[Co(lig)_2]X_2$ have magnetic moments which vary from 2.1 to 2.7 B.M. according to the anion (X) present in the salts. Stoufer, Basch, and Hadley[14] have drawn attention to the anomalous magnetic moments of complex cobalt(II) salts containing pyridine-2,6-dialdehyde-dihydrazone and have offered evidence that their salts are equilibrium mixtures of two spin states. It would seem more than likely that the compounds listed in Table V are similar mixtures of electronic isomers but this remains to be proved experimentally.

Conductivities.—Attention should be drawn to the fact that the molecular conductivities determined in nitrobenzene solution and listed in Tables II and IV are the normal expected values. In aqueous solution, however, large increases in conductivity occur. This may be attributed to the dissociation of protons from coordinated ligand residues in this solvent of high dielectric capacity (the ionic conductance of H^+ at infinite dilution at 25° is approximately 350 $ohm^{-1}/cm.^2$).

Spectra.—Comparison of visible spectra in aqueous ethanol solution (Table VII) of the above-described complexes clearly indicates that XXII ($[Co(H\text{-}lig\text{-}IV)_2](ClO_4)\cdot 2H_2O$) and XXIII ($[Co(H\text{-}lig\text{-}V)_2](ClO_4)_2$) lose one proton per complex cation upon solution in this solvent. The conductivities in aqueous solution would lead to an anticipation of this result, which is confirmed by the fact that, although the peaks in the visible are of an intensity typical of the type of resonating ring structure set up by deprotonation, these peaks are only approximately half as intense as the same visible peaks for the corresponding doubly-deprotonated complexes XXIX ($[Co(lig\text{-}IV)_2]\cdot 1.5H_2O$) and XXX ($[Co(lig\text{-}V)_2]\cdot H_2O$) in the same solvent.

The compounds $[Co(lig)(H\text{-}lig)](ClO_4)_2$ where the ligand is I or II, which lose one proton per complex cation in aqueous ethanolic solution, have ultraviolet–visible absorption spectra in this solvent which are identical with those of the corresponding doubly-deprotonated $[Co(lig)_2](ClO_4)$ compounds. The spectra are little affected by the addition of acid to the ethanolic solution, indicating disinclination toward reprotonation.

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[13] R. Hogg and R. G. Wilkins, *J. Chem. Soc.*, 341 (1962).

[14] R. C. Stoufer, D. H. Basch, and W. B. Hadley, *J. Am. Chem. Soc.*, **83**, 3732 (1961).