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Pentadentate Ligands. V. Cobalt(II) Complexes of the Linear Schiff Base Ligand Derived from 2-Pyridinecarboxaldehyde and Bis(3,3′-aminopropyl)amine

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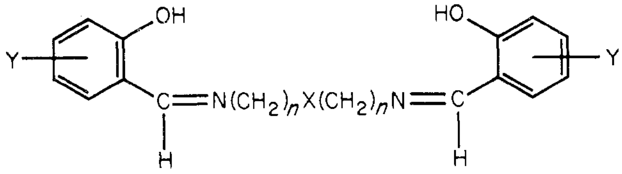
Cobalt(II) complexes employing the linear potentially pentadentate ligand derived from 2-pyridinecarboxaldehyde and bis(3,3′-aminopropyl)amine have been prepared. Complexes of general formula $[Co(pyDPT)X]X \cdot H_2O$ where $X^- = Cl^-$, Br^-, I^-, NO_3^-, and SCN^- have been isolated. Complexes of composition $[Co(pyDPT)](PF_6)_2$ and $[Co(pyDPT)(NCSe)]NCSe$ have also been prepared. All complexes have been characterized by infrared and visible spectral measurements, magnetic susceptibility, and conductometric measurements. The complexes are stable toward oxidation in the solid state but readily oxidize in solution. The chloride, bromide, and nitrate are extremely hygroscopic. The magnetic moments of these materials are functions of their extent of hydration. The thiocyanate and selenocyanate materials have intermediate magnetic moments in the solid state whereas the weaker ligands, iodide and hexafluorophosphate, show typical low-spin values. In solution the chloride, bromide, iodide, nitrate, and hexafluorophosphate derivatives exhibit magnetic moments in the range 1.9–2.5 BM while the thiocyanate material maintains its intermediate magnetic moment in solution. In the solid state the stronger field ligands are postulated to form six-coordinate pseudooctahedral species, while the iodide and hexafluorophosphate complexes are assumed to be five-coordinate. The anomalous magnetic properties of the stronger field ligands are interpreted in terms of a doublet–quartet spin-state equilibrium.

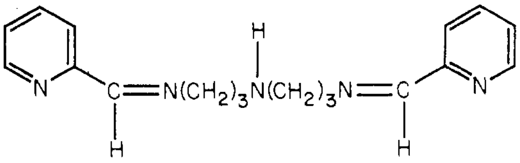
Introduction

The stereochemical consequences and extent of binding of linear potentially pentadentate ligands to transition metal ions are not well understood. Such factors as (1) flexibility of the ligand, (2) number of atoms between donor groups, and (3) metal ion involved have been demonstrated to be important in determining the arrangement of donor atoms about the metal ion. In many cases an intermediate geometry has been attained which represents a compromise between the coordinating requirements of the metal ion and the steric demands imposed by the ligand. The irregular geometry adopted often results in unusual magnetic properties for the complexes.

For example, ligands of type Ia are known to give high-spin five-coordinate complexes with manganese(II), iron(II), cobalt(II), nickel(II), and copper(II).[1] Ligands of type Ib yield (a) four-coordinate distorted square-planar nickel(II) complexes which possess anomalous magnetic properties,[2] (b) high-spin pseudotetrahedral cobalt(II) complexes,[3] and (c) seven-coordinate complexes with the uranyl ion in which the five donor atoms of the pentadentate ligand and uranium atom occupy the same plane.[4] Ligands of Ic are thought to give rise to (a) highly distorted five-coordinate nickel(II) complexes which also are magnetically anomalous[5] and (b) high-spin pseudotetrahedral cobalt(II) complexes.[3] Cationic nickel(II) complexes of the neutral pentadentate ligand derived from 2-pyridinecarboxaldehyde and bis(3,3′-aminopropyl)amine, II (hereafter referred to as pyDPT), have been shown to adopt exclusively a pseudooctahedral configuration in which each donor atom from the pentadentate ligand is bound to the nickel(II) ion as well as to an anion or molecule of solvent.[6] We wish to report here our results dealing with the cationic cobalt(II) complexes of this ligand.



Ia, $n = 3$, $X = NH$
b, $n = 2$, $X = NH$
c, $n = 2$, $X = S$



pyDPT
II

Experimental Section

Materials. 2-Pyridinecarboxaldehyde and bis(3,3′-aminopropyl)amine (DPT) were obtained from the Aldrich Chemical Co., Milwaukee, Wis. The 2-pyridinecarboxaldehyde was distilled *in vacuo* before using, collecting the fraction which boiled at 40–41° (5 mm). The compound KSeCN was obtained from Alfa Inorganics, Inc., Beverly, Mass. All other chemicals and solvents were of reagent grade or equivalent.

Preparation of $[Co(pyDPT)Cl]Cl \cdot H_2O$. To a stirred solution of 2-pyridinecarboxaldehyde (5.35 g, 0.05 mol) dissolved in 50 ml of absolute ethanol plus 3 ml of triethyl orthoformate was added DPT (3.28 g, 0.025 mol). The solution was refluxed under nitrogen for 10 min, turning from a pale yellow to a dull orange. To this refluxed solution was added dropwise and under nitrogen a solution prepared by adding $CoCl_2 \cdot 6H_2O$ (5.94 g, 0.025 mol) to a minimum amount of methanol plus 5 ml of triethyl orthoformate. The solution immediately became dark red and was refluxed under nitrogen for 50 min. Upon cooling the solution overnight, a dark red-brown material precipitated. The precipitate was recrystallized from hot methanol–ethanol and filtered in an inert atmosphere and dried *in vacuo* at 100° for 12 hr.

Preparation of $[Co(pyDPT)(NO_3)]NO_3 \cdot H_2O$. This material was prepared as described above with the minor modification that $Co(NO_3)_2 \cdot 6H_2O$ was substituted for $CoCl_2 \cdot 6H_2O$.

Preparation of the Iodide, Bromide, Thiocyanate, Selenocyanate, and Hexafluorophosphate Derivatives. The pentadentate ligand was preformed in the manner described above. To the refluxing solution of the ligand was added dropwise and under nitrogen a solution

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[1] L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, 88, 5180 (1966).

[2] W. M. Coleman and L. T. Taylor, *Inorg. Chem.*, 10, 2195 (1971).

[3] S. R. Edmondson, W. M. Coleman, and L. T. Taylor, 23rd Southeast Regional Meeting of the American Chemical Society, Nashville, Tenn., Nov 4–6, 1971.

[4] M. K. Akhtar, E. D. McKenzie, R. E. Paine, and A. J. Smith, *Inorg. Nucl. Chem. Lett.*, 5, 673 (1969).

[5] W. M. Coleman and L. T. Taylor, *J. Amer. Chem. Soc.*, 92, 1449 (1970); *J. Inorg. Nucl. Chem.*, 33, 3049 (1971).

[6] C. T. Spencer and L. T. Taylor, *Inorg. Chem.*, 10, 2407 (1971).

prepared by dissolving $Co(C_2H_3O_2)_2 \cdot 4H_2O$ in a minimum amount of methanol plus 5 ml of triethyl orthoformate. The solution immediately became dark red and was refluxed under nitrogen for 50 min. The resulting solution was allowed to come to room temperature and approximately 20 ml of a saturated solution of NaI, NaSCN, KSeCN, or NH_4PF_6 was added. Upon cooling overnight, a dark brown-red material precipitated. The products were recrystallized from hot ethanol or methanol-ethanol mixtures and isolated as described above.

Physical Measurements. Infrared absorption spectra in the region 5000–400 cm^{-1} were determined employing a Nujol or hexachlorobutadiene mull technique with a Perkin-Elmer Model 621 grating spectrophotometer and a Beckman IR-5A recording spectrophotometer.

Ultraviolet–visible–near-infrared spectra at room temperature were obtained using a Cary 14 recording spectrophotometer. Diffuse transmittance spectra were obtained using Nujol mulls supported on Whatman No. 1 filter paper.[7]

Magnetic susceptibility data were obtained at room temperature by the Faraday method using mercury(II) tetrathiocyanatocobaltate(II) and tris(ethylenediamine)nickel(II) thiosulfate as the calibrants. Diamagnetic corrections were made employing Pascal's constants.[8] Susceptibilities for paramagnetic species in solution were determined by the nmr method given by Evans[9] using a Varian A-60 spectrometer and a C-60H nmr spectrometer from Japan Electron Optics Laboratory Co., Ltd., equipped with a proton JNM-C-60H variable-temperature probe. Temperature control was maintained by a Varian Model V6040 or with a JEOLCO JES-VT-3 temperature controller.

Molar conductances were measured using a Barnstead Model PM-70CB conductivity bridge and a cell with a constant of 1.50 cm^{-1}. The deionized, distilled water and the nitromethane used for these measurements had specific conductances of less than 10^{-6} ohm^{-1}.

Thermal gravimetric analysis (tga) and differential thermal analysis (dta) in the temperature range 25–270° were performed using a Stone Model 3 instrument.

Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and in this laboratory, using a Perkin-Elmer Model 240 carbon–hydrogen–nitrogen analyzer.

Results and Discussion

Complexes of general formula $[Co(pyDPT)X]X \cdot H_2O$ where $X^- = Cl^-, Br^-, I^-, NO_3^-$, and SCN^- as well as [Co(pyDPT)(SeCN)]SeCN and $[Co(pyDPT)](PF_6)_2$ have been prepared. All the complexes are thought to be six-coordinate except for the I^- and PF_6^- derivatives which appear to be low spin and five-coordinate. Characterization through elemental analysis, solution, and solid-state magnetic measurements in addition to conductometric and spectral measurements has been carried out.

Analytical data for these new compounds are shown in Table I. Most of the subject complexes are powdery after drying but the bromide, selenocyanate, and nitrate are highly crystalline. The color of the complexes ranges from red to dark brown. All of the complexes are extremely soluble in cold water. They are slightly soluble in cold methanol, ethanol, dimethyl sulfoxide, pyridine, and nitromethane but dissolve readily upon heating in all listed solvents. They are insoluble in hot benzene, acetone, and chloroform. The complexes are thermally stable but melt above 200° with decomposition. Dta on the chloride, bromide, and iodide derivatives showed a very broad endothermic peak around 100°, which may correspond to the loss of water. The absence of a stepwise weight loss in the tga measurements up to 200° suggests that the water incorporated into the structure is water of hydration and not coordinated water.

In the solid state, the complexes appear to be fairly stable in air, at least for a small amount of time. However, prolonged exposure to the laboratory atmosphere causes the nitrate, bromide, and chloride to turn into a black, sticky tar. The other complexes also appear to be hygroscopic, but pick up water at a much slower rate than the above three. Reaction in the solid state with oxygen of the air has not been observed. In solution, all of the complexes are relatively unstable when exposed to air. When a small amount of any of the complexes is dissolved in water or methanol, the color of the solution turns quickly from a dark red-brown to a lighter brown. When air is bubbled through the solution, the color change occurs even more rapidly.

Conductance measurements in an inert atmosphere in deionized, distilled water at several concentrations were made. The measurements in open air showed only a slight change in molar conductance from those taken in an inert atmosphere although the solutions had discolored. In water most of the complexes behave as 2:1 electrolytes.[10] At concentrations approximately 0.001 *M* the iodide, bromide, chloride, nitrate, and thiocyanate complexes have molar conductances in the range 230–260 ohm^{-1} cm^{-1} mol^{-1}. The data suggest that at low concentrations extensive hydrolysis occurs with production of $[Co(pyDPT)(OH_2)]^{2+}$ in aqueous solution. The data in nitromethane indicate that the thiocyanate and selenocyanate derivatives are 1:1 electrolytes[11] ($\Lambda_m = 108$ ohm^{-1} cm^{-1} mol^{-1} for NCS^- (0.001 *M*) and $\Lambda_m = 115$ ohm^{-1} cm^{-1} mol^{-1} for $SeCN^-$ (0.006 *M*)). It is reasonable to assume that in both of these cases, instead of a nitromethane molecule, an anion is coordinated to the cobalt ion. On the other hand, the PF_6^- derivative ($\Lambda_m = 203$ ohm^{-1} cm^{-1} mol^{-1} (0.001 *M*)) is a 2:1 electrolyte which may be rationalized on the grounds that a solvent molecule has replaced a coordinated PF_6^- group or, more probably, that the cation in $[Co(pyDPT)](PF_6)_2$ is a five-coordinate complex which dissociates completely in nitromethane.

Infrared spectra were obtained on Nujol and hexachlorobutadiene mulls, Table II, and confirm pentacoordination of the organic ligand. The vibrational frequencies of the pyridine ring and the Schiff base linkage of the side chain are observed in the spectral region consistent with the proposed ligand formulation[12] and coordination of the azomethine linkages to the cobalt(II) ion. Unequivocal assignment of a band to the N-H stretching frequency for most of the complexes was made uncertain due to their being monohydrates as well as their extremely hygroscopic nature. Bands arising from water almost completely obscure the N-H stretching region for some of the complexes. Support for the N-H stretch assignment is found in the observation that lattice water[13] normally absorbs at 3550–3200 cm^{-1}. All hydrates show a band below 3200 cm^{-1}, in addition to broad absorption assignable to the presence of water. The question regarding coordination of the water and/or the secondary amine cannot unequivocally be answered without an X-ray study. Nevertheless, a few observations can be made. Free secondary aliphatic amines[14] normally absorb above 3200 cm^{-1}. Coordination should lower this stretching

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[7] R. H. Lee, E. Griswold, and J. K. Kleinberg, *Inorg. Chem.*, 3, 1278 (1964).

[8] B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. J. Wilkins, Ed., Interscience, New York, N. Y., 1960.

[9] D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

[10] 1:1 electrolyte, $\Lambda_m = 96$–115 ohm^{-1} cm^{-1} mol^{-1}; 2:1 electrolyte, $\Lambda_m = 225$–270 ohm^{-1} cm^{-1} mol^{-1}.

[11] In nitromethane: 1:1 electrolyte, $\Lambda_m = 85$–97 ohm^{-1} cm^{-1} mol^{-1}; 2:1 electrolyte, $\Lambda_m = \sim 177$ ohm^{-1} cm^{-1} mol^{-1}.

[12] The infrared spectra of similarly formulated complexes have been recently discussed. See ref 6.

[13] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley-Interscience, New York, N. Y., 1970, p 166.

[14] R. T. Conley, "Infrared Spectroscopy," 2nd ed, Allyn and Bacon, Boston, Mass., 1970.

Table I. Analytical Data for the Cobalt(II) Complexes

	Analyses, %							
	C		H		N		Halogen	
Compd	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
[Co(pyDPT)I]I·H_2O	33.75	33.91	3.90	3.53	10.93	10.63		
[Co(pyDPT)(NCS)](NCS)·H_2O	47.78	48.01	4.98	4.78	19.52	19.51		
[Co(pyDPT)(NCSe)]NCSe	41.52	41.13	3.94	3.96	16.95	16.99		
[Co(pyDPT)]$(PF_6)_2$	32.84	32.78	3.53	3.52	10.64	10.44		
[Co(pyDPT)Br]Br·H_2O	39.56	39.26	4.57	4.18	12.82	12.45	29.26	29.9
[Co(pyDPT)(NO_3)](NO_3)·H_2O	42.30	42.41	4.90	4.35	19.21	19.13		
[Co(pyDPT)Cl]Cl·H_2O	47.26	47.62	5.47	4.93	15.31	15.29	15.31	15.9

Table II. Infrared Spectra[a] (cm^{-1}) of the Cobalt(II) Complexes

			Pyridine ring			
Compd	N–H str[b]	C=N str	I	II	III	IV
[Co(pyDPT)I]I·H_2O	3100 b	1615 m	1595 s	1575 w	1475 m	1435 s
[Co(pyDPT)(NCS)](NCS)·H_2O	3160, 3120 m	1635 m 1640 m	1595 s	1565 w	1475 m	1435 s
[Co(pyDPT)(NCSe)](NCSe)	3180, 3140 m	1630 m	1595 s	1580 w	1480 m	1445 s
[Co(pyDPT)]$(PF_6)_2$	3280, 3250	1630 m	1595 s	1570 w	1480 m	1445 s
[Co(pyDPT)Br]Br·H_2O		1630 m	1605 s	1580 w	1480 m	1440 s
[Co(pyDPT)(NO_3)](NO_3)·H_2O	3140 b	1628 m	1600 s	1560 w	1480 m	1440 s
[Co(pyDPT)Cl]Cl·H_2O		1625 m	1595 s	1565 w	1475 m	1435 s
pyDPT	3200 b	1644 s	1587 s	1567 m	1468 m	1435 s

[a] Abbreviations used: s, strong; m, medium; w, weak; b, broad. [b] An accurate assignment for the N–H stretch in the bromide and chloride is not possible due to its being masked by the symmetric and asymmetric O–H stretches of water.

frequency. The fact that only [Co(pyDPT)]$(PF_6)_2$ has an N-H stretching absorption above 3200 cm^{-1} would suggest that the amine group is coordinated. Co(SALDPT), Ia, has an N-H stretch at 3250 cm^{-1} and is known to have a coordinated amine function.[14] Hydrogen bonding, however, between amine and a molecule of water or an anion could possibly produce the same observation. The employment of the 3500-cm^{-1} region to ascertain if water is coordinated or is simply water of hydration is ambiguous. The 800- and 540-cm^{-1} regions corresponding to the rocking and wagging vibrations, respectively, of the whole coordinated water molecule are thought to be more diagnostic.[15] Water of crystallization does not exhibit these vibrations. Vibrational overtones from the organic ligand prevented a definite assignment of bands due only to water in this region.

Many of the derivatives have anions which give infrared-active bands. For [Co(pyDPT)]$(PF_6)_2$, the infrared spectrum shows a very strong, broad band spanning the 900-800 cm^{-1} region. This band is assigned to noncoordinated hexafluorophosphate. No band is observed which can unequivocally be assigned to coordinated PF_6^-. In light of the extremely poor coordinating properties of PF_6^-, we have assumed neither PF_6^- anion is coordinated.

The ir spectrum of [Co(pyDPT)(NO_3)](NO_3)·H_2O shows a sharp band at 1745 cm^{-1}. This band is not found in the infrared spectrum of any of the other cobalt(II) complexes and is assigned as ionic nitrate.[16] Strong, broad absorption is observed in the region 1250-1400 cm^{-1}. The resolution in this band is very poor, regardless of the mulling agent. It is tempting to suggest that the absorption is due to both ionic and coordinated nitrate since both absorb in this region.[16]

In the complex [Co(pyDPT)(NCS)](NCS)·H_2O, two intense bands, both of which are split into two peaks, occur in the 2040-2075-cm^{-1} region. One of the major bands is located at 2055 and 2040 cm^{-1} (sh) and is assigned to an ionic thiocyanate C≡N stretch.[17] The maximum of the other major band occurs at 2075 and 2065 cm^{-1} (sh). This latter peak with its accompanying shoulder is assigned to coordinated thiocyanate, since C≡N stretching bands are usually shifted to higher frequencies upon coordination to a metal ion.[18] In addition the region 700-805 cm^{-1} contains two peaks, one at 745 cm^{-1} and the other at 805 cm^{-1}. The former band is attributed to the C-S stretch for ionic SCN^- and the latter band is assigned as the C-S stretch for coordinated SCN^-.[19,20] The positions of the band are also in the region expected for N-bonded thiocyanate.[21]

The infrared spectrum of [Co(pyDPT)(NCSe)](NCSe) shows bands at 2067 and 2055 cm^{-1} which are assigned as the ionic and coordinated C≡N stretching modes, respectively.[22] Bands at 510 and 520 cm^{-1} are assigned to a C—Se stretching mode for coordinated and ionic selenocyanate. The bands at 2055 and 510 cm^{-1} are consistent with N-bonded selenocyanate.[23]

Magnetic susceptibility data in the solid state and in solution for each of the derivatives are shown in Table III. The chloride, bromide, nitrate, thiocyanate, and selenocyanate derivatives exhibit in the solid state magnetic moments in the range 3.5-4.2 BM which may or may not be anomalous depending upon the true structure of each complex. The magnetic moment of the thiocyanate and selenocyanate complexes are unchanged upon standing in the air and upon recrystallization from a boiling solvent in an inert atmosphere. Three complexes, Cl^-, Br^-, and NO_3^-, are extremely hygroscopic which make it somewhat difficult obtaining magnetic susceptibility measurements especially since it was observed

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(15) K. Nakamoto, *Advan. Chem. Ser.*, **No. 62**, 399 (1967).

(16) N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, **4**, 804 (1965).

(17) N. F. Curtis and Y. M. Curtis, *Aust. J. Chem.*, **19**, 1423 (1966).

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

(22) A. E. Wickenden and R. A. Krause, *Inorg. Chem.*, **4**, 404 (1965).

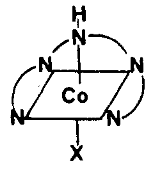
(23) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and T. E. Haas, *Inorg. Chem.*, **1**, 565 (1962).

Table III. Magnetic Data of the Cobalt(II) Complexes in Solution

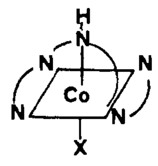
Compd	Solvent	T, °K	Concn, g/ml	$10^6 \chi_m$, cgsu	μ_{eff}, BM
$[Co(pyDPT)I]I \cdot H_2O$	Pyridine	298	0.02	1976	2.18
	Solid	296		1602	2.14
$[Co(pyDPT)(NCS)](NCS) \cdot H_2O$	Pyridine	293	0.02	5259	3.55
	Solid	298		5602	3.76
$[Co(pyDPT)](PF_6)_2$	Pyridine	293	0.02		1.95
	Solid	299		1180	1.91
$[Co(pyDPT)(NCSe)](NCSe)$	Solid	298		5355	3.59
$[Co(pyDPT)Br]Br \cdot H_2O$	Water	289	0.02	1632	1.95
	Solid	298		4253	3.69
$[Co(pyDPT)(NO_3)](NO_3) \cdot H_2O$	Water	289	0.02	1667	1.93
	Solid	298		7039	4.18
$[Co(pyDPT)Cl]Cl \cdot H_2O$	Water	289	0.02	2436	2.35
	Solid	297		7791	4.30

that the magnetic susceptibility is a function of the extent of hydration, decreasing as the compound picks up water. The decrease in μ_{eff} averaged approximately 2.5 BM over a 3-day period on replicate samples of each complex. Upon redrying each sample *in vacuo* at 100° the experimental moments return to near their original value. The I^- and PF_6^- complexes are not hygroscopic and have moments of 2.18 and 1.95 BM, respectively. Where solubility allowed, magnetic susceptibility measurements were also obtained in either water or pyridine, Table III. The solutions were prepared in an inert atmosphere (N_2) and placed in a special nmr coaxial tube which permitted only a minimum amount of exposure to the atmosphere during sample preparation and measurement. The calculated magnetic moments fall around 2.0 BM with the lone exception being the thiocyanate derivative.

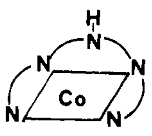
The magnetic properties of Co(II) complexes vary depending on the stereochemistry of the complex and the type of ligands involved,[24] and certainly the complexes reported herein are not exceptions to this rule. The magnetic data in Table III reveal that every derivative does not conform to the same spin type. It appears that the spin state is determined largely by the anion type, although other parameters such as the degree of hydration, coordination number, etc., may be just as important. In the solid state and in pyridine the hexafluorophosphate and iodide derivatives have moments around 2.0 BM, which may arise from a low-spin (1) cis or trans octahedral (IIIa, IIIb), (2) cis or trans five-coordinate, or (3) square-planar (IIIc) environment around cobalt(II). The last structure would come about from the secondary amine not coordinating. Since infrared evidence suggests that the secondary nitrogen is coordinated in all of the derivatives, the square-planar structure seems least likely in the solid state. In view of the stoichiometry of the hexafluorophosphate derivative, its visible spectra in the solid state (*vide infra*), and the very poor coordinating ability of PF_6^-, the complex is best thought of as a five-coordinate structure. Infrared and analytical data definitely show the presence of water in the iodide complex; therefore, the magnetic data may be rationalized in terms of a five- or six-coordinate low-spin complex with the latter being achieved by coordination of H_2O or I^- in the sixth position. A definite assignment cannot be made at this point.



cis-octahedral
IIIa

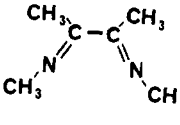


trans-octahedral
IIIb

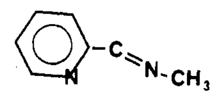


square planar
IIIc

The magnetic behavior of the remaining complexes is difficult to explain thoroughly. None of the moments fall in the range 4.8-5.28 BM which is typical of high spin octahedral cobalt(II). Only the Cl^- and NO_3^- complexes fall in the range for tetrahedral (4.2-4.8 BM) and five-coordinate square-pyramidal and trigonal-bipyramidal (4.2-4.6 BM) complexes.[25] Pentacoordination of the organic ligand would rule against the former. A five-coordinate structure can be eliminated as a possibility in light of their visible spectra (*vide infra*). The magnetic moments of all derivatives except I^- and PF_6^- apparently are anomalous assuming that the complexes are pseudooctahedral. Stoufer and coworkers[26-28] have reviewed the numerous mechanisms by which anomalous magnetic behavior in cobalt(II) complexes may arise. These workers have shown that many, if not all, pseudooctahedral complexes which show anomalous magnetic behavior are characterized by having ligands which possess the diimine linkage (*i.e.*, N=C–C=N). Structures IVa and b show some representative examples.[29] Temperature-dependent magnetic susceptibility studies on these materials have revealed them to be primarily spin-state isomers in which the quartet and doublet states are positioned approximately within thermal energy of each other.



biacetylmethylimine
IVa



2-pyridinalmethylimine
IVb

pyDPT is closely related to the ligand systems studied by Stoufer. The major difference is that in pyDPT pairs of diimine linkages are joined together by a seven-atom chain in which one of the atoms is a donor group (*i.e.*, a secondary nitrogen atom) whereas Stoufer's compounds have no chain of atoms joining the two normally coplanar diimine linkages. A study of stereomodels reveals that the two N=C–C=N linkages in pyDPT may coordinate in either a cis or trans coplanar manner to the cobalt(II) and at the same time allow the secondary nitrogen to span one of the axial sites.

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(25) E. K. Barefield, D. H. Busch, and S. M. Nelson, *Quart. Rev., Chem. Soc.*, 22, 457 (1968).

(26) R. C. Stoufer, *et al.*, *Inorg. Chem.*, 5, 1167 (1966).

(27) H. M. Fisher and R. C. Stoufer, *Inorg. Chem.*, 5, 1172 (1966).

(28) D. L. Williams, D. W. Smith, and R. C. Stoufer, *Inorg. Chem.*, 6, 590 (1967).

(29) These figures are rather simple illustrations of the diimine linkage. Other more complicated cases are $[Co(PdAdH)_2]I_2$, $[Co(terpy)_2](ClO_4)_2 \cdot H_2O$, and $[Co(PPMI)_2](ClO_4)_2 \cdot H_2O$, where PdAdH is 2,6-pyridinedialdihydrazone, terpy is 2,2'-terpyridine, and PPMI is 1,3-bis(2-pyridyl)-2-azapropane.

Consequently, it is not unreasonable to propose that the chloride, bromide, nitrate, thiocyanate, and selenocyanate derivatives are pseudooctahedral complexes in the solid state in which a quartet-doublet spin-state equilibrium exists.

The observation that very weak field ligands (PF_6^- and I^-) give low-spin complexes, whereas, stronger field ligands which give rise to higher magnetic moments may be attributed to several factors. Perhaps these low-symmetry complexes have the doublet state lying lowest, and with increasing axial perturbation the quartet state falls within thermal energy of the ground state and becomes partially occupied. Alternatively, the PF_6^- and I^- complexes may adopt a five-coordinate geometry in which the metal is low spin and the remaining derivatives form a six-coordinate structure possessing anomalous magnetic properties. In other words, these complexes may be near the borderline where six-coordinate, high-spin species are very similar in stability to low-spin species of reduced coordination number.[10,30] Finally, some unusual crystal effects in the solid state may account for these phenomena since the magnetic moments approached low-spin behavior as they absorb moisture but are anomalous when dry. A study of the magnetic susceptibility as a function of temperature is planned for these materials.

Magnetic moments for the Cl^-, Br^-, NO_3^-, and PF_6^- derivatives in aqueous solution and in pyridine for the I^- derivative are essentially identical and strongly suggest normal low-spin behavior. A satisfactory solvent could not be found for the $SeCN^-$ complex; and only pyridine proved to be adequate for the SCN^- material. The magnetic moment is unchanged upon dissolution in pyridine, indicating a relatively strong axial perturbation even in solution, where, no doubt, SCN^- or pyridine complete the octahedral structure. The moments for Br^-, NO_3^-, and PF_6^- are consistent with the values reported for low-spin penta- and hexacoordinated cobalt(II) but are lower than those generally reported for presumed square-planar cobalt(II).[31] On the other hand, the I^- complex in pyridine and the Cl^- in water have moments which fall in the range expected for square-planar cobalt(II).

The assumption of low-spin behavior in solution and upon increasing hydration by the Cl^-, Br^-, and NO_3^- derivatives may be attributed to a number of factors. Crystal packing effects may be causing the anomalous magnetism. A somewhat related dependence of the magnetic properties of bis(2,2′,2″-terpyridine)cobalt(II) complexes on the degree of hydration has been observed. Changes in the symmetry around the cobalt ion arising from the extent of hydration have been postualted to account for this phenomenon.[32] Magnetic susceptibility measurements on the cobalt(II) complexes of ligand type Ia have been shown to depend on the degree of hydration.[33] Alternatively, the coordinating affinity of the secondary NH group may become greatly reduced as a result of hydrogen bonding with water or pyridine in solution or in a highly hydrated state. This would drastically reduce the coordinating tendency of the secondary amine and weaken the overall effect of any axial perturbation by the secondary amine. In other words, a structure in solution approximating a square plane or a highly distorted square pyramid would be produced in which the doublet state constituted the lowest energy state. Some precedence for such a rationalization is found in the observation that five-coordinate $Ni(CR)Br_2 \cdot H_2O$[34] is surprisingly diamagnetic due to the weaker axial field of the lone coordinated bromide ion that arises from hydrogen-bonded interaction with a water molecule in the crystal.[35] A third but less likely explanation might be that a conversion from a trigonal bipyramid to a square pyramid may be occurring in going from the solid to solution. Although the number of known structures is small, it appears that trigonal-bipyramidal stereochemistries prevail in high-spin complexes, and square-pyramidal ones, in the low-spin case.[36]

Visible spectra in the solid state on Nujol mulls were measured in the region 5000-40,000 cm^{-1}. The spectra are not amenable to an obvious interpretation. In most cases a very broad band is observed in the solid state around 14,000 cm^{-1} which is not observed in solution spectra. Increasing absorption with decreasing wavelength characterizes each spectrum and may be attributed to one or more relatively low-energy charge-transfer bands that "tail off" into the visible region and may mask very weak d-d transitions. Superimposed on this absorption are several low-intensity ill-defined shoulders (16,000-25,500 cm^{-1}) some of which may be d-d transitions. In aqueous solution these shoulders are also not observed except for the one at *ca.* 23,000 cm^{-1}. Being low spin in solution any d-d transition no doubt is going to appear relatively high in energy and certainly will be observed by ligand-related transitions. Since magnetic measurements in the solid state strongly suggest that the complexes are near the crossover point, the ground state cannot be represented as a spin-doublet or spin-quartet and an interpretation in simple terms is not possible. It can be stated that the general features of our spectra are strikingly similar to the complexes of bis(2,2′,2″-terpyridine)cobalt(II) which have been found to be magnetically similar.

The spectrum of the PF_6^- derivative differs from the spectra of the other derivatives. A very prominent broad band is observed at 9000 cm^{-1}, and a broad band centered at 14,300 cm^{-1} which possesses weak but discernible fine structure is also seen. Busch and Long[37] have recently reported the spectra for a series of low-spin five-coordinate cobalt(II) complexes possessing four nitrogen donors in a macrocyclic ligand with an anion completing the pentacoordinate structure. A comparison of our spectrum and theirs reveals them to be almost identical. The iodide derivative exhibits a similar spectrum but the band intensity in the 9000-cm^{-1} region is considerably reduced. This observation provides further evidence in support of a five-coordinate structure for these two derivatives.

Registry No. pyDPT, 37805-58-6; $[Co(pyDPT)I]I \cdot H_2O$, 37768-67-5; [Co(pyDPT)(NCS)](NCS), 37805-28-0; [Co(pyDPT)(NCSe)](NCSe), 37807-74-2; $[Co(pyDPT)](PF_6)_2$, 37805-29-1; [Co(pyDPT)Br]Br, 37805-30-4; $[Co(pyDPT)(NO_3)](NO_3)$, 37805-31-5; [Co(pyDPT)Cl]Cl, 37805-32-6.

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