Contribution from the Department of Chemistry
Syracuse University, Syracuse, N. Y. 13210, U.S.A.

Magnetic and Spectral Studies of Some Five-Coordinate Mono(2, 2', 2",- terpyridine) Complexes of Co(II) and Ni(II)

J. S. Judge and W. A. Baker, Jr.

Received June 19, 1967

A number of five-coordinate mono(2,2′,2″-terpyridine) complexes of formula $M(terpy)X_2$ *[*M *= Co(II) or Ni(II);* $X = Cl^-, Br^-, I^-, NCS^-$ *and* NO_3^-*] have been prepared. Their reflectance spectra in the visible and near infrared regions have been obtained. These spectra exhibit as many as six absorption bands which may be attributed to d-d transitions. The magnetic behavior of these complexes has been studied over the range 15-400°K. Some of the magnetic moments are unusually high for such an asymmetric environment and remain high even at the lowest temperatures. An ordering of the d-orbitals based on the σ- and π-bonding abilities of the ligands is proposed to rationalize the observed spectral and magnetic results.*

Introduction

Though for some time five-coordinate structures involving first transition series ions were believed to be rare, in recent years many examples have been reported.[1] The tridentate ligand 2,2′,2″-terpyridine has been shown to form two types of coordination compounds with divalent first transition series ions-bis(terpyridine) compounds of empirical formula $M(terpy)_2X_2$ and mono(terpyridine) compounds, $M(terpy)X_2$.[2] Corbridge and Cox[3] showed by x-ray analysis that the compounds $Zn(terpy)Cl_2$ and $Zn(terpy)I_2$ were five-coordinated structures which they represented as a distorted trigonal bipyramid. Gerloch[4] has recently reinterpreted their data as best representing a square pyramidal stereochemistry and Einstein and Penfold[5] have refined the original data continuing to represent the molecules as a trigonal bipyramid. Some of the compounds $M(terpy)X_2$ with M = Mn, Fe, Co and Ni and X = Cl, Br, I, SCN have been shown to be five-coordinate, primarily through their isomorphism with the analogous zinc compounds.[6]

Recently Lions, Dance and Lewis[7] have reported the spectral and magnetic properties of a series of mono-chelate complexes of pyridine-2-aldehyde 2′-pyridylhydrazone. Some of these complexes have been shown to be five-coordinate square pyramids. They also included the terpyridine complexes $Co(terpy)Cl_2$ and $Ni(terpy)Cl_2$ which they interpreted as square pyramids. They indicate that square pyramidal symmetry for Co^{2+} is consistent with a high, temperature indepedent magnetic moment ($\sim$5.0 B.M.) and by electronic absorption in the region 11,000-14,000 cm^{-1} (as well as approximately 4 or 5 other absorptions which they observed).

We describe here the preparation and properties of a series of mono(terpyridine) complexes of empirical formula $M(terpy)X_2$. Some such compounds have been shown clearly not to be five-coordinate, but are cation-anion species or bridging structure.[8] The compounds $M(terpy)X_2$ with M = Co and X = Cl, Br, I, SCN and M = Ni and X = Cl, Br, I are five-coordinate,[6] as may be the mono(terpyridine) cobalt nitrate. For these compounds it is worthwhile to consider qualitatively whether their spectral and magnetic properties are more in keeping with a square pyramidal or a trigonal bipyramidal approximation.

Experimental Section

Preparation of Compounds. $Co(terpy)Br_2$ and $Ni(terpy)Br_2$. These compounds were prepared by heating the corresponding bis complexes in vacuum.[9] *Anal.* Calcd. for $Co(terpy)Br_2$: C, 39.86; H, 2.45; N, 9.30. Found: C, 40.09; H, 2.82; N, 9.69. Calcd. for $Ni(terpy)Br_2$: C, 39.87; H, 2.45; N, 9.30. Found: C, 39.69; H, 2.61; N, 9.10.

$Co(terpy)Cl_2$ and $Ni(terpy)Cl_2$. Although heating in vacuum has been previously used[9] to prepare these compounds, a new wet method was used in this instance (a sample of the cobalt compound was also prepared by thermal decomposition in vacuum). In this method, 1.5 mmoles of terpyridine and 1.9 mmoles of MCl_2 were dissolved in a 60-40% by volume water-methanol solution. The solution was evaporated to near saturation ($\sim$15 cc) and 70 cc of acetone added. A precipitate then formed which was filtered, washed with water, and dried in vacuum. *Anal.* Calcd. for $Co(terpy)Cl_2$: C, 49.61; H, 3.05; N, 11.57. Found for the sample prepared by thermal decomposition in vacuum: C, 49.91; H, 3.32; N, 11.54. Found for the

---

(1) For pertinent references see E. L. Muertterties and R. H. Schunn, *Quart. Rev.*, XX, No. 2, 245 (1966).

(2) G. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1649 (1937).

(3) D. E. C. Corbridge and E. G. Cox, *J. Chem. Soc.*, 594 (1956).

(4) M. Gerloch, *J. Chem. Soc.*, Part A, 1318 (1966).

(5) F. W. B. Einstein and B. R. Penfold, *Acta Cryst.*, *20*, 92 (1966).

(6) J. S. Judge, W. R. Reiff, G. Intille, P. Ballway and W. A. Baker, Jr., *J. Inorg. Nucl. Chem.*, 29, 1711 (1967).

(7) F. Lions, I. G. Dance and J. Lewis, *J. Chem. Soc.*, Part A, 565 (1967).

(8) J. S. Judge and W. A. Backer, *Inorg. Chim. Acta*, *1*, 245 (1967).

(9) R. Hogg and R. G. Wilkins, *J. Chem. Soc.*, 57, 341 (1962).

sample prepared by the wet method: C, 49.96; H, 3.10; N, 11.69. Calcd. for Ni(terpy)Cl_2: C, 49.64; H, 3.06; N, 11.58. Found: C, 49.87; H, 3.25; N, 11.60.

Co(terpy)I_2 and Co(terpy)$(NCS)_2$. These complexes were prepared by heating the corresponding bis complexes in vacuum to somewhat higher temperatures (210-225°C) than the corresponding bromides. *Anal.* Calcd. for Co(terpy)I_2: C, 32.99; H, 2.03; N, 7.70. Found : C, 33.29; H, 2.26; N, 7.95. Calcd. for Co(terpy)$(NCS)_2$: C, 50.00; H, 2.72; N, 17.15. Found: C, 50.37; H, 2.75; N, 17.52.

Ni(terpy)I_2. This compound was never prepared in sufficient purity for other than x-ray work. The bis-terpyridine nickel iodide was heated to 300°C in vacuum for several days. *Anal.* Calcd. for Ni(terpy)I_2: C, 33.0; H, 2.04; N, 7.70. Found: C, 35.2; H, 2.24; N, 8.43.

Co(terpy)$(NO_3)_2$. Terpyridine (1.5 mmoles) and Co$(NO_3)_2$ (2.1 mmoles) were dissolved in 25 cc of CH_3OH. The solution was filtered to remove any undissolved material, and was then evaporated to $\sim$20 cc at which point 60 cc of acetone were added. A pink flocculent precipitate formed and increased as the solution was evaporated to $\sim$5 cc. Then 15 cc more of acetone was added, the suspension filtered, the precipitate washed with acetone and dried in vacuum. *Anal.* Calcd. for Co(terpy)$(NO_3)_2$: C, 43.28; H, 2.66; N, 16.83. Found: C, 43.63; H, 2.77; N, 16.78.

Physical Measurements. Infrared spectra were obtained in KBr pellets using a Perkin-Elmer 521 grating spectrophotometer. Electronic spectra were obtained using a Cary Model 14 with a Cary Model 1411 Diffuse Reflectance Accessory. $MgCO_3$ was used as the reference.

Magnetic measurements were performed on a Faraday type balance which used a Varian 4 inch electromagnet and associated power supply and regulator. The pole caps were the constant force type and gave a force constant to 1% over 4 mm. vertical distance. The balance used was a Cahn Model RG recording electrobalance. The sample size was of the order of 50 mg. which resulted in forces of 1-20 mg. All measurements were made at three different field strengths and no field dependence was observed. The sample was cooled using a Gifford-McMann gas balancing, two stage refrigeratore manufactured by Cryomech Corp. of Syracuse, N. Y. The refrigerator is capable of operation over the range of 15-300°K.

Results and Discussion

Infrared Spectra. Co(terpy)$(NCS)_2$ exhibits a strong, broad CN absorption at 2072 cm^{-1} with a shoulder at 2023 cm^{-1}. In addition a medium intensity peak is observed at 821 cm^{-1} due to the C-S stretch and the NCS bending absorption is observed at 474 cm^{-1}. All of these absorptions are in the regions characteristic of terminal N-bonded thiocyanate.[10]

The spectrum of Co(terpy)$(NO_3)_2$ contains several bands due to the nitrate ion. There is a strong peak at 1382 cm^{-1}, the asymmetric stretch, which is indicative of an ionic nitrate ion. In addition, however, there are bands at 1491 and approximately 1300 cm^{-1} which can be attributed to the asymmetric stretch of a bonded nitrate.[11] The exact position of the latter cannot be determined since it overlaps a weak terpyridine band. The symmetrical stretch which is not infrared active unless the nitrate group is coordinated appears as a medium weak absorption at 1030 cm^{-1}. These data clearly indicate two types of nitrates in the compound, one ionic and one coordinated (in addition the compound is readily soluble in water, indicative of its ionic nature). Depending on whether the coordinated nitrate is mono- or bidentate the compound may be either four or five-coordinate. Unfortunately it is impossible to distinguish these two cases from infrared evidence.[11]

Eelectronic Spectra. The near infrared and visible absorption in reflectance of the mono(terpyiridine) complexes of cobalt are shown in Figures 1-3. It is apparent that the spectra of the cobalt compounds are quite complex, exhibiting a rather large number of absorptions, generally five or six, which can be ascribed to d-d transitions. Some of these are superimposed on the tail of an intense charge transfer band from the ultraviolet region. Any absorptions which occur

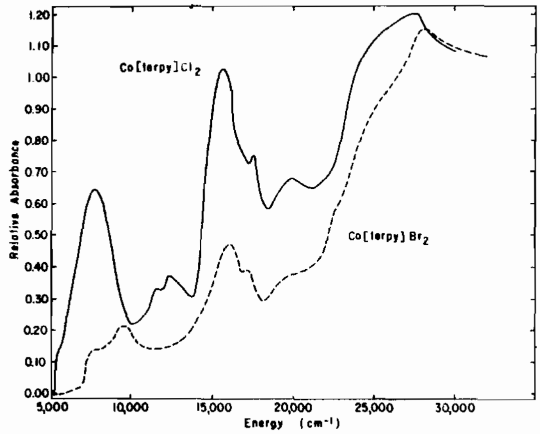

Figure 1. Reflectance spectrum of Co(terpy)Cl_2 (———) and Co(terpy)Br_2 (— — —).

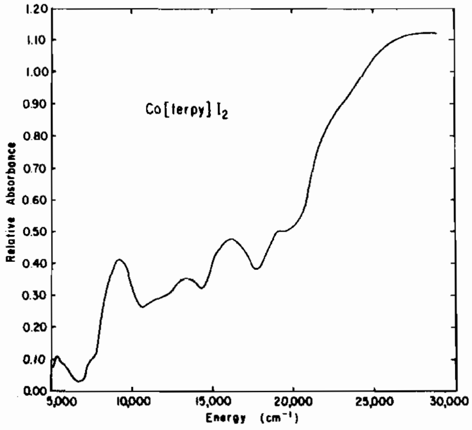

Figure 2. Reflectance spectrum of Co(terpy)I_2.

---

(10) A. Sabitini and I. Bertini, *Inorg. Chem.*, *4*, 1667 (1965).

(11) F. A. Cotton, D. M. L. Goodgame and R. H. Soderberg, *Inorg. Chem.*, *2*, 1162 (1963).

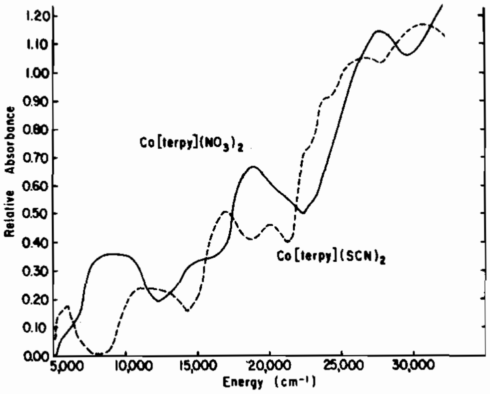

Figure 3. Reflectance spectrum of Co(terpy)$(NO_3)_2$ (———) and Co(terpy)$(SCN)_2$ (— — —).

above $\sim$25,000 cm^{-1} cannot be attributed to d-d transitions but are probably due to this charge-transfer band. The peculiarly shaped absorption which appears for the same complexes at 5,000-6,000 cm^{-1} (and only as a shoulder in others) is undoubtedly an overtone of a ligand vibrational band.

It was necessary to obtain reflectance spectra because of the general insolubility of the cobalt complexes and the fact that their five-coordinate nature is apparently altered in solution. The cobalt complexes generally dissolved only slowly, exhibiting at the same time a gradual increase in brown-red color characteristic of the bis(terpyridine) cation. The nickel complexes were soluble in methanol without any change from their characteristic green color. However, the spectra in solution differed from the solid state spectra. The iodide, bromide and chloride all give essentially the same spectrum in methanol (ν_1 = 10,900 cm^{-1}, ε = 24), whereas they differ in the solid state. This indicates that the solvent is replacing the halogens and that they are probably octahedral in solution since by a consideration of average environment one would expect ν_1 for three MeOH's and one terpyridine to be approximately

$$\tfrac{1}{2}[\nu_{(6H_2O)} + \nu_{(2\,terpy)}] = 10{,}600\ cm^{-1}$$

A similar result was observed for aqueous solutions of Ni(terpy)Cl_2 by Lions, *et al.*[7]

Mono(terpyridine) cobalt halides. The spectra of the five-coordinate chloride, bromide and iodide mono(terpyridine) cobalt complexes in Figures 1 and 2 show great similarity. The chloride, which is the best resolved, shows two split peaks at $\sim$12,000 cm^{-1} and $\sim$16,000 cm^{-1} between two unsplit peaks at $\sim$8,000 and $\sim$20,000 cm^{-1}. The iodide has a very similar pattern with the splitting in the peak near 16,000 cm^{-1} being unresolved. The bromide however, though very similar to the chloride in other respects, does not have an intense peak at 5,000-10,000 cm^{-1}. The observed split peak at 8,000-10,000 cm^{-1} may be a super-position of ν_1 and ν_2, ν_3; it may be that ν_1 occurs at lower energy in the bromide or that the peak in the 12,000 cm^{-1} region is just unresolved from the background. Considering the comparison of the spectrum of the iodide and chloride, the latter of these possibilities seems more likely.

In addition, it is apparent from the high energy bands that the observed spectrum is not particularly sensitive to variation in the halide ligands. The spectrum of the chloride clearly indicates that under conditions of good resolution, six absorptions should be observed.

Co(terpy)$(NCS)_2$. The spectrum of the five-coordinate thiocyanate in Figure 3 shows five peaks or shoulders in this same region. The lowest energy absorption at 11,000-13,000 cm^{-1} is very broad and probably conceals two unresolved peaks. The peculiarly shaped peak at 6,000 cm^{-1} is a good example of the previously mentioned vibrational overtone that is more or less regularly observed in the spectra of these complexes in the 5,000-6,000 cm^{-1} region. This is probably the cause of the slight shoulders observed in many of the other spectra on the low-energy side of the peaks in this region.

Co(terpy)$(NO_3)_2$. The spectrum of the mono(terpyridine) cobalt nitrate is also shown in Figure 3. The low energy band appears similar in shape to that of the thiocyanate. There are apparently only two more absorptions visible, however. Thus the spectrum does not appear to be that of a five coordinate complex unless there are additional bands at higher energies which are hidden by the charge transfer bands. Actually, the spectrum resembles those normally observed for tetrahedral complexes, the broad band at 9,000 cm^{-1} being ν_2 and the two peaks at 14,900 and 18,800 cm^{-1} being a split ν_3 band. This is a rather large splitting of ν_3 for tetrahedral cobalt since the values of $\Delta\nu_3$ are normally about 2,000 cm^{-1}. The observed splitting of the ν_3 band for unsymmetrical tetrahedral complexes has been observed, however, to be somewhat larger.[12] The spectrum does in fact agree reasonably well with that expected from the complete energy level diagram published by Liehr[13] if one assumes Dq to be 550 cm^{-1}.

Mono(terpyridine) nickel halides. The spectrum of the mono(terpyridine) nickel chloride and bromide are very similar. Both show a shallow band with a maximum at 5,400 cm^{-1} and a broad flat band which appears to contain at least two and possibly three superimposed peaks in the region 10,000-14,000 cm^{-1}. This latter group is at slightly higher energy in the bromide than in the chloride.

In a trigonal bipyramid arrangement the order of one electron orbital splittings is not expected to be altered even when the five ligands may be of significantly different type. However, in a square pyramid arrangement the order of the one-electron orbitals as well as their energies may be altered when the identity of all the ligands is not the same and when π bonding effects are included.

Complete energy level diagrams for nickel in the field of five equivalent dipoles in both trigonal and square pyramidal symmetry have been reported.[14] A similar diagram for Co^{2+} in trigonal bipyramidal symmetry has also been published.[15] These diagrams are not very useful in interpreting the above spectra, though

---

(12) F. A. Cotton, O. D. Faust, D. M. L. Goodgame and R. H. Holm, *J. Am. Chem. Soc.*, 83, 1780 (1961).

(13) A. D. Liehr. *J. Phys. Chem.*, 67, 1314 (1963).

(14) M. Ciampolini, *Inorg. Chem.*, 5, 35 (1966).

(15) M. Ciampolini, N. Nardi and G. P. Speroni, *Coord. Chem. Rev.*, *1*, 222 (1966).

they were useful in fitting the spectra of these author's compounds, cobalt and nickel complexes of bis(2-dimethylaminoethyl)methylamine and tris(2-dimethylaminoethyl)amine. With these aliphatic ligands, their weak field assumptions and exclusion of π bonding effects were appropriate. It is doubtful these assumptions would be applicable to terpyridine complexes.

More appropriate for a qualitative picture of the spectra to be observed in the square pyramid approximation is a treatment similar to that done by McClure[16] for non-cubic ions taking into account the relative π and σ bonding strengths of the different ligands. Assuming a perfect square pyramid arrangement with an X group occupying the axial position, the energies of the one electron orbitals in terms of σ and π antibonding strength of the ligands N and X become as shown in Table I. When exchange and interelectronic repulsion are included this treatment predicts six observable spin allowed one-electron d-d transitions for Co^{2+} and Ni^{2+}. Transitions from (dyz, dxy, to dxz are not included since it is assumed that these will occur at energies too low to be observed. In addition, for Co^{2+} it predicts two widely separated bands with two split bands in between. For Ni^{2+} it predicts two groups of three bands each being split by 5,000-10,000 cm^{-1} depending on the relative values of σ_N, σ_X, π_N, π_X and the Racah parameter B. The energies of these transitions are shown in Table II. This is in contrast ot the trigonal bipyramid arrangement in which one expects no more than 3 such transitions for Co^{2+} and no more than 4 for Ni^{2+}.

Table I. Energy of the One-Electron Orbitals in Square Pyramidal

M(terpy)X_2 Complexes [a]	
$d(x^2-y^2)$	$\sigma_X+3\sigma_N$
dz^2	$5/3\,\sigma_X+\sigma_N$
dxz	$2\,\pi_X+\pi_N$
dyz, dxy	π_X

[a] The results are obtained by assuming the X groups to be on the z and x axes and the nitrogens from the terpyridine on the x and y axes. No allowance was made for the fact that the structure is not a perfect square pyramid.

The observed spectra for the five-coordinate cobalt complexes agree qualitatively very well with the predicted spectral pattern for the square pyramid arrangement. The spectra show six transitions in the predicted pattern (see particularly the spectrum of the mono(terpyridine) chloride in Figure 1). There are certainly more than the two or three transitions predicted in the trigonal bipyramid approximation. As far as the mere number of transitions is concerned, of course, this would be a reflection of the fact that the symmetry of the molecule is in reality less than that of a perfect trigonal bipyramid. Nevertheless, the degree of separation of the four major bands and the agreement of the observed and predicted pattern of the spectrum for a square pramid seem to favor this interpretation.

In like fashion the spectra of the nickel complexes seem to agree qualitatively with the prediction of the square pyramid treatment which would predict, as observed, two widely spaced groups of superimposed bands. This is particularly apparent in the higher energy band which is practically flat from 10,000 to 14,000 cm^{-1} in both the chloride and bromide. As such it is undoubtedly a group of overlapping bands.

Magnetic Properties. The magnetic moments of these mono(terpyridine) complexes at several temperatures are listed in Table III. These moments appear unusually high for such an asymmetric arrangement of ligands, which one would expect to a first approximation completely to quench any orbital contribution to the moment. In addition, they show surprisingly little temperature dependence, most of them remaining significantly above the spin-only value even at 20°K. At 20°K the chloride has a moment of 4.73 which is significantly higher than the moments predicted at this temperature for even weak field octahedral complexes.

There are two mechanisms by which orbital contribution can arise in the presence of a crystal field -- either through incomplete lifting of the free ion degeneracy in the ground state as occurs in octahedral complexes with generacy in the t_{2g} set or by spin-orbit coupling between the ground state and a near by excited state which «mixes in» some orbital contribution. If only a single excited state were of any significance, the moment in the latter situation would be of the form

Table II. Expected Energies of Observable Spin-Allowed One-Electron Transitions for Co^{2+} and Ni^{2+} in Square Pyramidal Stereochemistry

	Co^{2+}			Ni^{2+}		
	Transition	Excited State Configuration	E	Transition	Excited State Configuration	E
1	$xz \rightarrow z^2$	xy, z^2	$5/3\sigma_x+\sigma_N+\lvert\pi_N\rvert-2\pi_x-3B$	$xz \rightarrow z^2$	xz, x^2-y^2	$5/3\sigma_x+\sigma_N+\lvert\pi_N\rvert-2\pi_x+3B$
2	$xz \rightarrow z^2$	yz, z^2	$5/3\sigma_x+\sigma_N+\lvert\pi_N\rvert-2\pi_x+6B$	$xz \rightarrow x^2-y^2$	xz, z^2	$\sigma_x+3\sigma_N+\lvert\pi_N\rvert-2\pi_x+9B$
3	$xz \rightarrow x^2-y^2$	xy, x^2-y^2	$\sigma_x+3\sigma_N+\lvert\pi_N\rvert-2\pi_x+9B$	$xy \rightarrow z^2$	xy, x^2-y^2	$5/3\sigma_x+\sigma_N-\pi_x+12B$
4	$xz \rightarrow x^2-y^2$	yz, x^2-y^2	$\sigma_x+3\sigma_N+\lvert\pi_N\rvert-2\pi_x$	$xy \rightarrow x^2-y^2$	xy, z^2	$\sigma_x+3\sigma_N-\pi_x$
5	xy or $yz \rightarrow z^2$	xz, z^2	$5/3\sigma_x+\sigma_N-\pi_x+6B$	$yz \rightarrow z^2$	yz, x^2-y^2	$5/3\sigma_x+\sigma_N-\pi_x+3B$
6	xy or $yz \rightarrow x^2-y^2$	xz, x^2-y^2	$\sigma_x+3\sigma_N-\pi_x$	$yz \rightarrow x^2-y^2$	yz, z^2	$\sigma_x+3\sigma_N-\pi_x+3B$

---

(16) D. S. McClure, «Advances in the Theory of Coordination Compounds», Macmillan, New York, p. 498 (1961).

$\mu_{\text{spin-only}}\ (1 - \dfrac{x\lambda'}{\Delta E})$ where x is a small positive numer, λ' is the spin-orbit coupling constant and ΔE is the separation between the ground state and the higher state concerned. In addition this situation is accompanied by a temperature indepedent paramagnetism which is of the form $\dfrac{yN\beta^2}{\Delta E} = \dfrac{0.261y}{\Delta E(\text{cm}^{-1})}$, where y is a small positive number.

Table III. Effective Magnetic Moments at Several Temperatures for the Compounds $M(\text{terpy})X_2$

	μ_{eff} (B.M.)						
	$Co(\text{terpy})X_2$					$Ni(\text{terpy})X_2$	
T(°K)	Cl	Br	I	NCS	NO_3	Cl	Br
20	4.73	4.32	4.12	4.09	3.95		2.94
30	4.79	4.46	4.27	4.21	4.12		2.98
60	4.83	4.58	4.51	4.32	4.31		3.07
120	4.85	4.71	4.62	4.42	4.43	3.22	3.14
240	4.85	4.91	4.75	4.53	4.49	3.33	3.18
300	4.86	5.00	4.79	4.57	4.50	3.36	3.19
350	4.89	5.05	4.79			3.37	

Diamagnetic corrections used were ($\times 10^6$ cgsu): Co^{2+}, 12.8; Ni^{2+}, 12.8; Cl^-, 23.4; Br^-, 34.6; I^-, 50.6; NCS^-, 31.0; NO_3^-, 18.9; terpy, 148.

Making the assumption that the second case is the source of the high moments in these compounds, the TIP can be evaluated graphically at high temperature by plotting χ_M vs. $1/T$ and extrapolating to $1/T = 0$. The slope of such a plot yields the value of the temperature independent moment. From these values a Curies-Weiss law Θ can be evaluated. Table IV contains these values for the above complexes. The values of Θ are quite small as they must be if the assumption of constant moment is justified. That they differ from zero somewhat significantly, could be ascribed to errors in the measurements and the presence of low energy field components which become of importance at low temperature.

Table IV. Magnetic Data for the Normal Compounds of Empirical Formula $M(\text{terpy})X_2$ Assuming a Temperature Independent Magnetic Moment

Sample	Θ	TIP (10^6)	μ_{eff}	$\mu\text{-}\mu_{(\text{spin-only})}$
$Co(\text{terpy})Cl_2$	−0.6	200	4.91	1.03
$Co(\text{terpy})Br_2$	−3.7	1,400	4.67	0.79
$Co(\text{terpy})I_2$	−4.4	1,100	4.55	0.67
$Co(\text{terpy})(NCS)_2$	−3.0	900	4.35	0.47
$Co(\text{terpy})(NO_3)_2$	−3.9	550	4.37	0.49
$Ni(\text{terpy})Cl_2$	−5.0	330	3.25	0.42
$Ni(\text{terpy})Br_2$	−2.0	320	3.08	0.25

The last entry in Table IVis the value of $\mu\text{-}\mu_{\text{spin-only}}$. This decreases in the order $Cl > Br > I_2 > NCS > NO_3$ for the cobalt complexes and is less for the nickel complexes. The value of the TIP is in the same direction with the exception of the chloride. Neglecting the data on the chloride at the present, one can estimate the value of y/x which should be constant for the complexes of the same metal ion containing the same set of energy levels. The respective values of this ratio for the Br^-, I^-, NCS^- and NO_3^- of cobalt are 4,0, 3.8, 4.3, and 2.5. Thus a value of 4 is apparently typical of the five-coordinate complexes. The value of the nitrate is quite close to the theoretical value of 2 for tetrahedral complexes.

If the nitrate is indeed tetrahedral, one can calculate the value of 10Dq from its moment by the relationship given in reference (17). Assuming $\lambda' = 150\ \text{cm}^{-1}$, this yields a value of 4,800 cm^{-1} in fairly good agreement with the value of 5,500 cm^{-1} estimated from the spectrum and Liehr's diagram, considering in fact, the approximate nature of all of these relationships. On the basis of the infrared, electronic and magnetic data it would appear therefore that the nitrate can be described as a tetrahedral complex, although it is undoubtedly greatly distorted.

The trend in the values of $(\mu\text{-}\mu_{\text{spin-only}})$ indicates that ΔE, the separation between the ground and the first excited state increases in the order $Cl < Br < I < NCS$. This trend is easily understandable in terms of the square pyramid approximation by reference to the orbital splittings in Table I. The relevant ΔE here is the first separation $|\pi_N|\text{-}\pi_X$. (π_N will be negative while π_X is usually positive). It is well known that insofar as certain properties are concerned, the π donating power of these ligands decreases in the above order which would increase ΔE as observed (consider for example their relative activating power in nucleophilic aromatic substitution).

---

(17) F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *J. Am. Chem. Soc.*, 83, 4690 (1961).

The low value of the TIP for the chloride and its high low- temperature moment may be rationalized in this picture as follows. The chloride will have the highest value of π_x so the separation $|\pi_N|$-π_x apparently becomes so small that the approximation of $\lambda \ll \Delta E$ is no longer valid. The situation becomes somewhat analogous to the t_{2g} set in the octahedron, three nearly degenerate orbitals split by spin-orbit coupling. This, however, is not a completely analogous situation and the normal spin-orbit splitting of the octahedral ground stante which results in the lowest J state being of lowest energy would not necessarily be observed. A high moment at low temperature in this qualitative picture is therefore not necessarily unexpected.

Lions, Dance and Lewis[7] have indicated that for square pyramidal cobalt(II) the observed magnetic moments are usually higher when the symmetry in the basal plane is higher. These results do not appear to agree with this generalization; e.g., compare μ for Co(terpy)(NCS)$_2$. In addition this treatment predicts a higher moment for ligands with the greatest difference in their π bonding. However, as this difference increases it tends to increase the degeneracy in the π bonding orbitals which is, in a sense, equivalent to increasing the degree of symmetry.

In the trigonal bipyramidal approximation the first excited state coresrponds to an unpaired electron in the e′ and e″ set. This state could mix some orbital contribution into the ground level.

The observed values of μ-$\mu_{o.s.}$ for Co^{2+} in Table IV however, show clearly that ΔE would have to increase in the order Cl < Br < I < NCS for this interpretation to hold. In a trigonal bipyramid arrangement the dxz, dyz set should be little affected by π bonding and are lowest in energy because they are not σ bonding. The d(x^2-y^2), dxy set seems unlikely to have a significant π involvement and is essentially σ bonding. Consequently, assuming the σ effect is dominant, they should be raised in energy relative to the dxz, dyz in the order of the spectrochemical series. That is, ΔE would be the reverse of the above, at least for the halogens. (The position of the thiocyanate is correct in either approximation.)

The other interpretation, that is that the ground state has a temperature dependent moment, could not be valid for cobalt in the trigonal bipyramid approximation since the ground state is not orbitally degenerate. In the approximation of square pyramidal symmetry, however, the unpaired electron in the dxy, dyz set in the ground state may have orbital angular momentum associated with it. Thus the degeneracy would be lifted by spin-orbit coupling giving rise to a temperature dependent moment.

As mentioned above, the separation between the dxz and the dzy, dyz set is only $|\pi_N|$-π_x. If this value approaches zero as it may for a strong π donor such as chloride ion, a situation resembling the t_{2g} set of the normal octahedral case arise. This situation is well known to give rise to orbital contributions of up to 1.4 Bohr magnetons. This could also be qualitatively the explanation for the observed decrease in moment which is in the order of decreasing π_x.

The isostructural nickel complexes exhibit only a small excess over their spin-only moments. This also is more consistent with the square pyramid approximation. Again the order chloride to bromide is somewhat inconsistent with excited state contributions in trigonal bipyramids. In the d^8 system the trigonal bipyramid rather than the square pyramid would be the one expected to have a significant orbital contribution in the ground state.

It appears therefore that the magnetic data definitely favor the square pyramid approximation for these five-coordinate compounds. The origin of the orbital contribution to the observed moments can be viewed either way and as ΔE approaches the order of λ, as is the case of the chloride, the distinction between these views becomes somewhat meaningless.

Acknowledgements. The authors are grateful to the National Science Foundation for support of this work.