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

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Received June 19, 1967

Mono(2,2',2"-terpyridine) complexes of formula M(terpy)X_2 with M = Co(II), X = CN, NO_2 and F and with M = Ni(II), X = CN and SCN have been prepared. Their spectra in the visible, near infrared and infrared regions have been obtained. The magnetic behavior of these compounds has been studied over the range 15-400°K. These data indicate that the compounds are not five-coordinate but are cation-anion species involving in each case a bis(terpyridine) cation (with the exception of Ni(terpy)$(SCN)_2$ which contains bridging thiocyanate groups). The anions in the case of the two cyanides are shown to be the square planar $M(CN)_4^{2-}$. The $(CoF_4)^{2-}$ anion is best interpreted as a tetrahedral ion. The evidence suggests that the anion in the nitrite compound involves a dimeric structure with bridging nitrite groups.

Introduction

In the course of the investigation of an extensive series of 1:1 complexes of 2,2',2"-terpyridine (hereafter terpyridine or terpy) with cobalt(II) and nickel(II)[1,2] a number of compounds were prepared which had the empirical formula M(terpy)X_2, but whose properties indicate that they are not simple five-coordinate structures. Compounds of this empirical formula were first prepared and described by Morgan and Burstall.[3] Some of these compounds, particularly those in which X = halogen, have been shown to be five-coordinate.[1,2,4] The properties of those compounds in which the anion X has a strong tendency to bond to the metal (e.g. CN, NO_2) indicate that they are not five-coordinate.

Experimental Section

Preparation of Complexes. Co(terpy)$(CN)_2$ and Ni(terpy)$(CN)_2$. These compounds were prepared by the addition of a KCN solution to a solution of $Co(terpy)_2^{2+}$ Since the exact procedure is somewhat critical, particularly in the case of the cobalt compound, it shall be described in detail. For both cobalt and nickel, 2.1 mmoles of MCl_2 and 4.0 mmoles of terpyridine were heated in 60 cc of distilled water. To this 5 cc of a 1 *M* KCN solution was added. An immediate precipitate forms. In the case of the nickel compound this solution was filtered, the precipitate rinsed with water, dried overnight in vacuum, and finally heated for several hours to ~80°C at 25μ pressure.

The preparation of the cobalt compound followed initially the same steps except that after the addition of the KCN solution the resulting suspension was boiled for several hours. During this time the brown-yellow precipitate redissolved. Then the solution was evaporated to ~20 cc and cooled, at which point a reddish-brown precipitate formed. This precipitate was filtered, washed with water and dried in vacuum. It was then heated in vacuum to 140°C for one hour to remove any excess terpyridine. *Anal.* Calcd. for Co(terpy)$(CN)_2$: C, 59.32; H, 3.22; N, 20.35. Found: C, 59.45; H, 3.22; N, 20.16. Calcd. for Ni(terpy)$(CN)_2$: C, 59.35; H, 3.22; N, 20.36. Found: C, 58.93; H, 3.59; N, 19.85.

Co(terpy)$(NO_2)_2$. No precipitation was effected by the direct addition of NO_2^- to a solution of Co$(terpy)_2Cl_2$. Therefore, a yellow nitrite of cobalt was prepared by heating a concentrated solution of KNO_2 and $CoCl_2$. Five millimoles of terpyridine (a definite excess, since a noticable amount did not go into solution) were reacted with 0.3 grams of this insoluble yellow nitrite in 25 cc of distilled water at ~90°C for 1/2 hour. The solution as then cooled and filtered to remove the excess terpyridine. Then the solution was evaporated to ~4 cc to effect precipitation of the reddish-brown complex. This was later recrystallized again from water and dried in vacuum. It was then heated overnight in vacuum (~100μ) at 120°C. There was no change in appearance. *Anal.* Calcd. for Co(terpy)$(NO_2)_2$: C, 46.89; H, 2.89; N, 18.23. Found: C, 46.70; H, 3.02; N. 18.04.

Co(terpy)F_2. The bis compound (prepared by the addition of terpyridine to CoF_2) was heated in vacuum at 160°C for two hours. *Anal.* Calcd. for Co(terpy)F_2: C, 54.56; H, 3.36; N, 12.73. Found: C, 54.47; H, 3.40; N, 12.53.

Ni(terpy)$(SCN)_2$. The bis compound was prepared by the addition of KSCN to an aqueous solution of $Ni(terpy)_2(NO_3)_2$. The resulting light brown compound was heated for four hours at 210°C in a vacuum

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(2) J. S. Judge and W. A. Backer, *Inorg. Chim. Acta*, *1*, 239(1967).
(3) G. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1640 (1937).
(4) D. E. C. Corbridge and E. G. Cox, *J. Chem. Soc.*, 594 (1954).

of ~100μ. During this time the compound becomes a greenish yellow. This material was removed from the vacuum and heated in 70 cc of water. The remaining bis is dissolved and a green precipitate of the desired complex remains as a precipitate. This was filtered, washed with water and methanol and dried in vacuum. *Anal.* Calcd. for Ni(terpy)$(SCN)_2$: C, 50.03; H, 2,72; N, 17.16. Found: C, 50.05; H, 2.59; N, 17.38.

Physical Measurements. Infrared spectra were obtained using a Perking-Elmer 521 grating spectrophotometer. Electronic spectra were obtained using a Cary Model 14 equipped with a Diffuse Reflectance accessory (Cary Model 1411) utilizing $MgCO_3$ as the reference material. Magnetic measurements were obtained on a Faraday type balance which has been previously described.[2] All measurements were obtained at three different fields and no field dependence was observed. X-ray powder data were obtained using nickel filtered CuK_α radiation.

Results and Discussion

Infrared Spectra. The infrared spectrum of mono(terpyridine) nickel thiocyanate exhibits a C≡N stretching absorption at 2117 cm^{-1} (s) and at 2096 cm^{-1} (vs). In addition the C-S stretching vibration appears at 799 cm^{-1} (w) and δ NCS at 449 cm^{-1} (w). This high value of the C≡N stretch coupled with the high value of the C-S stretch suggest the presence of bridging thiocyanates.[5]

The mono(terpyridine) nickel cyanide exhibits only one CN stretching vibration at 2117 cm^{-1} (vs) and the isomorphous cobalt compound only one at 2108 cm^{-1} (vs). Magnetic evidence indicates that the square planar anion $Ni(CN)_4^{2-}$ may be present in the nickel compound. Whereas in five-coordinate structures two cyanide stretching vibrations should appear, only one is expected for the square planar arrangement.[6].

The spectrum of Co(terpy)$(NO_2)_2$ has two bands at 1420 (mw) and 1220 cm^{-1} (vs) due to the NO stretching vibration. In addition a weak band appears at 450 cm^{-1} which may be ascribable to a metal nitrogen vibration indicating the presence of some N-bonded nitrite groups. A very weak absorption appears at 812 cm^{-1} in the region of the NO_2 bending mode. The position of the ν(NO) absorptions is not typical of terminal bonded nitro or nitrito groups. In particular the lower energy vibration observed falls clearly between the regions previously observed for terminal N-bonded and terminal O-bonded nitrite.[7] Therefore this would appear to indicate the presence of a bridging nitrite group.

Electronic Spectra. The reflectance spectra of these compounds are listed in Table I. In addition the spectra of the nitrite and fluoride are shown in Figure 1. All of these absorptions are superimposed on the tail of a charge transfer band which becomes completely dominant in the spectrum above about 25,000 cm^{-1}. Those absorptions reported here are only those which appear to be due to d-d transitions.

Table I. Visible and Near Infrared Reflectance Spectra

	ν (cm^{-1})
Ni(terpy)$(CN)_2$	12,700; 18,000; 22,700
Ni(terpy)$(SCN)_2$	11,600; 12,500 (sh); 17,200
Co(terpy)$(CN)_2$	14,500 (sh); 18,000 (sh); 19,600 (sh); 22,000
Co(terpy)$(NO_2)_2$	14,500 (sh); 18,000 (sh); 19,600
Co(terpy)F_2	6,500 (sh); 8,100; 13,600 (sh); 16,000 (sh); 17,400 (sh); 22,700

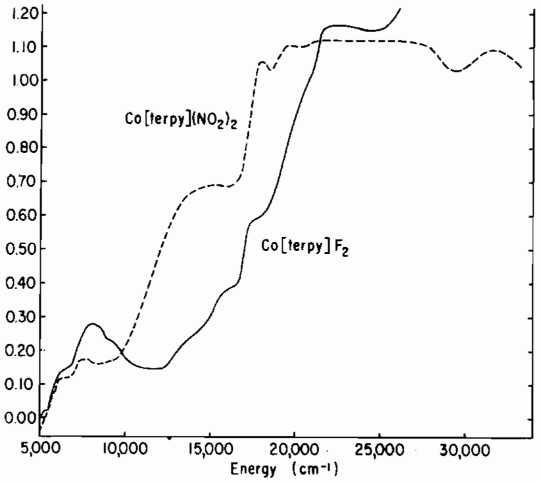

Figure 1. Reflectance spectrum of Co(terpy)F_2 (———) and Co(terpy)$(NO_2)_2$ (— — —).

The spectra of Co(terpy)$(CN)_2$ and Co(terpy)$(NO_2)_2$ are essentially the same as that of the species $Co(terpy)_2^{2+}$ both in reflectance and in solution.[8] The spectrum of Ni(terp)$(CN)_2$ is the same as that of the species $Ni(terpy)_2^{2+}$ which shows the same three peaks.[9] This strongly suggests that these three compounds are cation-anion species containing a bis(terpyridine) metal(II) cation and an anion of such a form that its absorptions occur at higher energy and are therefore masked by the charge transfer bands. If the two cyanide anions are formulated as square planar this would probably be true (the first intense absorption for square planar $Ni(CN)_4^{2-}$ occurs as a shoulder at 30,500 cm^{-1} on a peak at 32,500 cm^{-1}).[10]

In the case of mono(terpyridine) cobalt fluoride it was necessary to obtain a reflectance spectrum since the spectrum changes in solution.

The spectrum of the fluoride in Table I and Figure 1 can be interpreted in terms of a bis(terpyridine) cation and a tetrahedral fluoride anion. The cation absorption at 14,500 cm^{-1} is split by a superimposed portion of ν_3 of the anion. In addition, the peak at 18,000 cm^{-1} is shifted to a shoulder at 17,500 cm^{-1} by this superposition. This gives a value of ν_3 of the anion of

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(10) H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, *85*, 260 (1963).

~16,600 cm^{-1}. The value of the first peak at 8,100 cm^{-1} would be attributed to ν_2. Cotton and Goodgame[11] have correlated these values of ν_2 and ν_3 and the resulting parameters 10Dq and B for series of well-known tetrahedral cobalt complexes including the other halides. Following the same procedure, this assignment gives Dq = 486 and B = 695 for $(CoF_4)^{2-}$. These values fit in quite well with those observed for the other complexes. The value of 476 for Dq would be slightly larger than one might anticipate, though it is certainly a reasonable value inasmuch as one would expect Dq to decrease in the order F > Cl > Br > I and to be near the value of OH^- and NCS^- (423 and 455 cm^{-1}).

$Ni(terpy)(SCN)_2$ was insoluble in the common solvents. Its reflectance spectrum is quite different from those of the mono(terpyridine) nickel chloride and bromide which through the x-ray data have been shown to be five-coordinate. Liehr and Ballhausen[12] have published a complete energy level diagram for nickel in an octahedral field including spin-orbit coupling. The spectrum of this thiocyanate fits quite well to an octahedral pattern as interpreted from this diagram for 10Dq = 11,300 cm^{-1}. The first band predicted then is the transition $^3\Gamma_5 \rightarrow {}^3\Gamma_J$ (J = 2,3,4,5) at 11,300 cm^{-1}. The second is a transition to a singlet, $^1\Gamma_J$, which gains intensity because it has some triplet character mixed in through spin-orbit coupling. This would occur at 12,600 cm^{-1}. The third transition is to a group of triplet levels, $^1\Gamma_J$ (J = 1,3,4,5) at 17,500 cm^{-1}. It is apparent that the predicted spectrum for an octahedral environment falls very close to the observed spectrum for this compound. It is also obvious that Dq is less than that of $Ni(terpy)_2^{2+}$.

Magnetic Properties. The effective magnetic moments (in Bohr magnetons) for these compounds are listed in Table II. The moments observed for the two isomorphous cyanide compounds are below the spin only moments for the high spin state of these ions and above the moments observed for low-spin states. Assuming the anion is a square planar cyanide it should be diamagnetic in the case of the nickel ion. Then calculation of the effective moment of the cation yields a value of 3.01 at 150°K and 3.12 at 350°K. This is quite close to the moments observed for $Ni(terpy)_2^{2+}$ (3.00 at 150°K and 3.17 at 350°K) and therefore supports the interpretation of the compounds as a cation-anion species.

Table II. Effective Magnetic Moments at Several Temperatures

	Ni (terpy)X_2		Co (terpy)X_2		
T (°K)	SCN	CN	CN	NO_2	F
20	3.80		2.18	1.33	
30	3.69		2.25	1.33	3.16
60	3.46		2.36	1.34	3.26
120	3.28	2.11	2.45	1.36	3.71
240	3.31	2.19	2.69	1.69	4.08
300	3.34	2.21	2.79	2.04	4.16
350	3.39	2.22	2.90		

Diamagnetic corrections used were (×10^6 cgsu): SCN^-, 31.0; CN^-, 13.0; F^-, 9.1; NO_2^-, 17.7.

A similar calculation can be done for the cobalt compound by assuming a moment of 2.2 for the square planar anion. This leads to a value for the bis(terpyridine) cation moment which rises from 2.1 at 20°K to 3.6 at 400°K. This is reasonable since this cation exhibits a high spin-low spin equilibrium,[8] and also supports the formulation of these two compounds as cation-anion species with square planar anions.

The moment of $Ni(terpy)(SCN)_2$ shows a slight drop as the temperature is lowered below room temperature and then a gradual increase below about 100°K. Because the infrared may indicate a bridging SCN, it would appear reasonable that this compound is some sort of polymer. Since the moment rises as the temperature is lowered, it must posses ferromagnetic coupling between nickel atoms.

Fitting the data to a dimer or trimer with positive coupling (*i.e.*, with the S = 2 or S = 3 state lowest) was attempted but the experimental moment would have to increase much faster than is observed to fit these models.

If one assumes that the slight increase in moment observed between 100 and 400°K is associated with TIP of 4.50 . 10^{-6}, a plot of $1/(\chi_M' - 450 \times 10^{-6})$ versus temperature (see Figure 2) yields a straight line with an intercept at +7°K. Then the observed behavior is described by a Curie-Weiss Law and

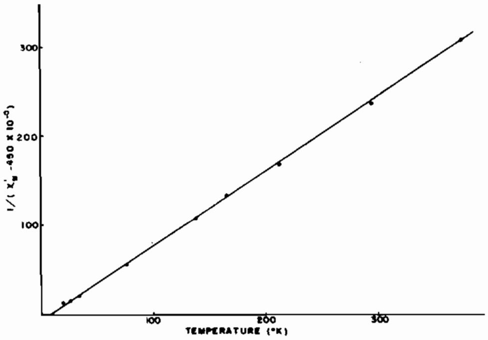
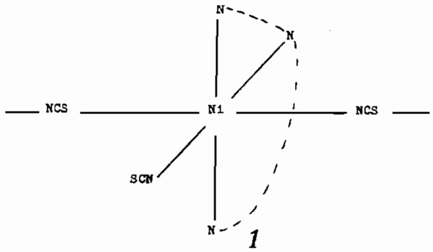


Figure 2. Plot of $1/(\chi_M' - 450 \times 10^{-6})$ vs. temperature for $Ni(terpy)(SCN)_2$.

$$\mu = 2.84\,[(\chi_M' - 450)(T - 7.2)]^{1/2}$$

where χ_M' is the observed molar susciptibility corrected for the diamagnetism of the ligands. This apparently indicates a true Curie point type of behavior. Thus the true formula for this compound would be $[Ni(terpy)(SCN)_2]_n$ where n is a large number. The above formula for μ yields a value of 3.12 which is close to that expected for octahedral nickel. The nickel atom could achieve octahedral coordination through one bridging SCN^- group per metal atom as in structure *1*. (The bridging groups could of course be *cis* and not *trans* as shown).



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

(12) A. D. Lieher, and C. J. Ballhausen, *Ann. Phys.*, N.Y., 6, 134 (1959).

It is interesting to note that a similar suggestion was made for the structure of $Ni(paphy)(NCS)_2$ by Lewis, Dance and Lions.[13] Unfortunately their magnetic data did not extend to sufficiently low temperatures to observe any incdease in moment which might be expected.

The moments of $Co(terpy)(NO_2)_2$ and that of $Co(terpy)F_2$ as a function of temperature are shown in Figure 3. The nitrite moment drops from 2 at room temperature to a constant value of 1.33 below about 70°K. The spectra of this compound indicated the presence of a bis(terpyridine) cation. This is quite conclusive. The moment of a bis(terpyridine) cation would level off to 1.87. Then the anionic species would have a moment given by

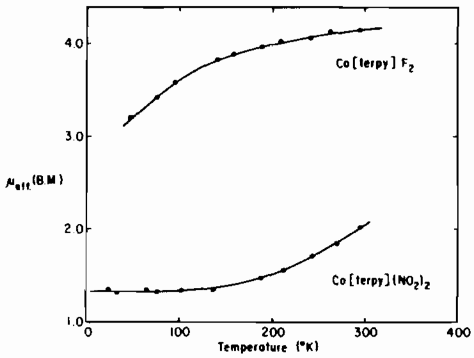
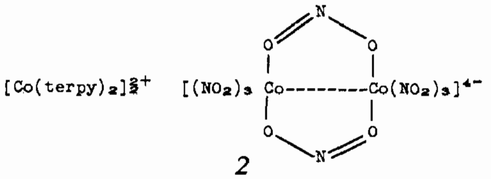


Figure 3. Plot of the effective magnetic moments vs. temperature for $Co(terpy)(NO_2)_2$ and $Co(terpy)F_2$.

$$(1.33)^2 = \frac{(1.87)^2 + \mu^2_{anion}}{2}$$

or $\mu_{anion} = 0$.

Therefore the anion must be at least a dimer, and considering the infrared evidence, must contain some kind of bridging nitrite. A possible structure to explain these properties would be as shown in sructure 2.



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The structure of the anion is certainly not conclusive, especially since little evidence for terminal nitrites was observed in the infrared spectrum. There are many other possibilities involving more complex structures and large numbers of cobalt atoms.

The spectra of the $Co(terpy)F_2$ was interpreted in terms of a bis-cation and a tetrahedral fluoride anion. The moment of the anion can be calculated as indicated in reference 11, giving a value of 4.38. Therefore one can calculate the apparent moment of the anion as a function of temperature as $\mu_{anion} = 2.84\,(\chi_M'T)^{1/2}$ where χ_M' is given by the relationship:

$$4.38 = 2.84\,[((\chi_M' - 440.10^{-6})(T - \Theta)]^{1/2}$$

Assuming $\Theta = -8°$ (Θ is generally $-4 \rightarrow -10°$ for these tetrahedral cobalt compounds) the moment of the bis-cation can be estimated. This yields a value of 2.0 at 50°K increasing to 3.9 at 300°K, again consistent with the high spin-low equilibrium behavior to be expected for the cation.[7] Thus the magnetic and spectral evidence both support the idea that this compound is $[Co(terpy)_2]^{2+}[CoF_4]^{2-}$ with the anion being tetrahedral.

Conclusion

The compounds $Co(terpy)(CN)_2$, $Ni(terpy)(CN)_2$, $Co(terpy)F_2$ and $Co(terpy)(NO_2)_2$ are proposed to be cation-anion species, in each case the cation being the metal bis(terpyridine) ion. The anion in the case of the two cyanides is apparently square planar. The $(CoF_4)^{2-}$ ion is best interpreted as a tetrahedral ion analogous to the other tetrahedral halides of cobalt(II). The structure of the anion in the nitrite cannot be definitely inferred but the evidence suggests a dimeric structure with bridging nitrite groups.

The compound $Ni(terpy)(SCN)_2$ is best represented as a polymeric $[Ni(terpy)(SCN)_2]_n$ with thiocyanate bridges and exhibits a ferromagnetic Curie point at ~7°K.

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

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