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Transition Metal Complexes of 2,2′,2″-Terpyridine 1,1′,1″-Trioxide

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Received July 18, 1969

The synthesis and characterization of a series of complexes of 2,2′,2″-terpyridine 1,1′,1″-trioxide (terpyO_3), a potentially tridentate ligand capable of forming seven-membered chelate rings, are reported. The compounds have been studied using electronic, infrared, and Mössbauer spectroscopy as well as magnetic susceptibility, X-ray powder pattern, and conductivity measurements. terpyO_3 acts as a very weak tridentate ligand and forms a series of bis and mono complexes with Co^{2+}, Ni^{2+}, Cu^{2+}, and Fe^{3+} and bis complexes of Fe^{2+} and Mn^{3+} as well as a mono complex with Mn^{2+}.

Introduction

The coordination properties and complexes of pyridine N-oxide,[2,3] 2,2′-bipyridine 1,1′-dioxide[4-6] (bipyO_2), and several other aromatic N-oxides have been studied extensively and recently reviewed.[7] In these systems it was found that coordination occurs through the oxygen atoms, and for bipyO_2 seven-membered metal chelate rings were obtained. To our knowledge no complexes of the ligand terpyO_3 have been previously reported. By analogy with bipyO_2, if all three oxygens of terpyO_3 coordinate, a complex containing two seven-membered chelate rings for each terpyO_3 is expected. Complexes containing seven-membered chelate rings are rare.[8-10] However, if the ligand involved assumes a suitable geometry, stable complexes can be formed. In the case of terpyO_3, a scale molecular model shows that the free ligand cannot be planar while the "parent" ligand 2,2′,2″-terpyridine is planar.[11] The lack of planarity for the trioxide is due to the steric interaction of the oxygens and probable repulsion of the lone electron pairs on them. A model tetrahedral coordination system containing one terpyO_3 and a monodentate ligand, *e.g.*, Cl^-, shows the central pyridine N-oxide bent well out of the plane formed by the other two. This apparently gives a compromise between steric interaction and bond angle strain in the ligand and complex as a whole. Attempts to make the foregoing four-coordinate system square planar result in severe strain of the aromatic ring system. The possibility of forming five-coordinate complexes containing one terpyO_3 and two monodentate ligands is not ruled out using models. However, there is only indirect evidence for such a structure in one complex of the present investigation. Coordination by all six oxygens of two terpyO_3 ligands is expected to result in formation of highly distorted pseudooctahedral systems. Molecular models and the results of this work confirm this expectation.

Experimental Section

Materials.—Analytical grade metal salts were used without further purification. The ligand terpyO_3 was prepared by the method of Case.[12]

Preparation of Complexes.—terpyO_3 is quite soluble in hot water. However, in order to avoid hydrolysis and competition of water with terpyO_3, most preparations were carried out in ethyl alcohol. The bis Cu^{2+}, Co^{2+}, Ni^{2+} perchlorate complexes were prepared by formation of a heated slurry of the ligand (2–3 mmol) in 50–100 ml of 95% ethyl alcohol. To this was added (in one portion) an alcohol solution containing a slight excess of hydrated metal perchlorate salt. In such a medium all of the ligand dissolved and the solid metal complex formed immediately. The mixture was refluxed with stirring overnight. The products were filtered from the hot mixture and washed with several portions of absolute ethyl alcohol and dried *in vacuo*. The same procedure was used in the preparation of $Fe(terpyO_3)_2(ClO_4)_2 \cdot 3H_2O$ except that the reaction was carried out under a nitrogen atmosphere to prevent oxidation.

The complex $Fe(terpyO_3)_2(ClO_4)_3 \cdot H_2O$ was prepared by dissolving 2.5 mmol of terpyO_3 in 45 ml of boiling water. To this solution was added the stoichiometric amount of $Fe(ClO_4)_3 \cdot 6H_2O$ dissolved in 10 ml of warm water. A red-yellow solution formed and on cooling yielded the desired product as fine crystals. The product was washed with small portions of cold water and alcohol and then dried.

The method of preparation of $Mn(terpyO_3)_2(ClO_4)_3$ was essentially that used by Nyholm and Turco[13] to prepare $Mn(bipyO_2)_3(ClO_4)_3$.

The complex $Ni(terpyO_3)_2Cl_2 \cdot 5H_2O$ was the result of an attempt to prepare a mono(nickel chloride) complex from a solution of the ligand and anhydrous metal chloride. terpyO_3 (3.2 mmol) and $NiCl_2$ (4.0 mmol) were found to dissolve very slowly in 550 ml of hot 1:1 absolute ethanol–methanol. The mixture was therefore refluxed overnight under dry nitrogen, the volume was decreased to 150 ml, and the mixture was then cooled in an ice bath. However, no solid could be isolated. Since the mono(nickel chloride) complex $Ni(terpyO_3)Cl_2 \cdot 0.5H_2O$ was obtained using an alcohol solution of hydrated nickel chloride, a small volume (10 ml) of water was added. The solution was then refluxed for 2 hr more and the volume was reduced to 100 ml. On cooling in an ice bath, the bright yellow $Ni(terpyO_3)_2Cl_2 \cdot 5H_2O$ resulted. The exact reasons for the formation of the bis complex are not clear, but apparently a more polar medium favors such a complex.

The mono-terpyO_3 complexes of Ni^{2+}, Cu^{2+}, and Mn^{2+} were

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TABLE I
ANALYTICAL DATA

Complex	% found			% calcd			Color
	C	H	N	C	H	N	
terpyO_3	63.96	4.18	15.08	64.05	3.95	14.91	White
Cu(terpyO_3)$Cl_2 \cdot 0.5H_2O$	42.81	2.93	10.02	42.42	2.85	9.99	Pale yellow
Cu(terpyO_3)$_2$(ClO_4)$_2$	43.79	2.82	10.02	43.67	2.69	10.19	Pale yellow
Ni(terpyO_3)$Cl_2 \cdot 0.5H_2O$	42.94	2.78	9.90	42.90	2.89	10.01	Bright green
Ni(terpyO_3)$_2Cl_2 \cdot 5H_2O$	45.91	3.94	10.73	46.06	4.13	10.75	Bright yellow
Ni(terpyO_3)$_2$(ClO_4)$_2 \cdot 2H_2O$	41.92	2.78	9.82	42.08	3.07	9.81	Bright yellow
Fe(terpyO_3)$_2$(ClO_4)$_2 \cdot 3H_2O$[a]	41.34	2.56	9.69	41.35	3.25	9.65	Light green
Fe(terpyO_3)Cl_3	40.62	2.51	9.48	41.35	2.70	9.44	Mustard yellow
Fe(terpyO_3)$_2$(ClO_4)$_3 \cdot H_2O$	38.01	2.31	8.96	38.54	2.59	8.99	Pale yellow
Co(terpyO_3)$_2$(ClO_4)$_2$	44.91	2.74	10.49	43.92	2.71	10.49	Olive green
Co(terpyO_3)$Cl_2 \cdot 0.5H_2O$	42.79	2.94	9.80	42.88	2.88	10.00	Light green
Mn(terpyO_3)$Cl_2 \cdot 3H_2O$	39.00	2.71	8.96	39.06	3.72	9.11	Bright orange
Mn(terpyO_3)$_2$(ClO_4)$_3$	40.20	2.66	9.42	39.34	2.43	9.17	Black

[a] Per cent Fe: calcd, 6.41; found, 6.80.

prepared using essentially the same method as for the bis complexes. A slight excess of hydrated metal chloride in alcohol solution was added to a heated ligand slurry and the desired product began to form immediately as the ligand dissolved. Such a mixture was refluxed for several hours and filtered while hot. The products were then washed with anhydrous alcohol and dried in a vacuum desiccator. The bright orange Mn^{2+} complex decomposed readily in light to a greenish black substance, and, hence, this system had to be stored in a light-free vacuum desiccator. Similar instability was observed for Mn(bipyO_2)$_3$(ClO_4)$_2 \cdot H_2O$.[4] In the cases of the mono complexes of Fe^{3+} and Co^{2+}, anhydrous metal salts were used in the preparations although no special precautions were taken to keep the reaction medium anhydrous. The analytical data for all of the preparations are given in Table I. The results are generally quite good for the formulations given. Exceptions are the manganese compounds which, due to both the method by which they were prepared and their general instability, are not unexpected. Where water of hydration is indicated, the amount is that which best fits the analytical results, but the presence and in a rough sense the amount of water are confirmed by the infrared spectra.

Analyses.—Carbon, hydrogen, nitrogen, and iron microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Infrared Spectra.—Infrared spectra were obtained using a Perkin-Elmer 521 grating spectrophotometer on finely ground samples suspended in a KBr matrix or mulled with mineral oil.

Electronic Spectra.—Solution spectra were obtained using a Cary Model 14 spectrophotometer while reflectance spectra were determined using a Cary 14 with a Cary 1411 diffuse reflectance attachment. The reference material used was $MgCO_3$. Spectral parameters Dq and B were determined graphically for the octahedral Co^{2+} and tetrahedral Ni^{2+} systems using the method outlined by Figgis.[14] The values of Dq and B for the octahedral Ni^{2+} and tetrahedral Co^{2+} complexes were calculated using the method given by Drago.[15]

Magnetic Measurements.—Magnetic susceptibilities were obtained by the Gouy method on apparatus previously described.[16]

Mössbauer Spectra.—The Mössbauer spectrometer was that used in a previous investigation.[17]

X-Ray Diffraction Measurements.—X-Ray diffraction patterns were obtained using a General Electric XRD-6 unit with nickel-filtered copper Kα radiation or iron-filtered cobalt radiation.

Results and Discussion

Infrared Spectra.—For the systems of this investigation the formation of complexes with oxygen coordination is most directly indicated by their infrared spectra. The free ligand has a strong asymmetric band at 1267 cm^{-1} and one at 1235 cm^{-1}. By comparison to bipyridine N-oxide[5] and pyridine N-oxide[18] these are assigned to N–O stretching vibrations. Similarly, the free ligand shows strong absorptions at 858 and 845 cm^{-1} which are attributed to N–O bending modes.[5] The "parent" ligand terpyridine exhibits a very complex infrared spectrum,[19] and, hence, the above assignments for terpyO_3 are not above question. However, terpyridine and terpyO_3 have essentially the same infrared spectra except for the regions 1200–1300 and 800–900 cm^{-1}, in which only weak to medium bands are observed for terpyridine thus lending confidence to the preceding assignments. The free oxide ligand also has medium bands at 335 and 368 cm^{-1} making the assignment of metal–oxygen stretching vibrations for the complexes difficult in most cases.

In terpyO_3 complexes there are three strong absorptions between 1200 and 1300 cm^{-1}. These quite likely correspond to the free ligand N–O stretch at 1235 cm^{-1} which is split in the complexes. The center of these bands in the complexes, 1220 cm^{-1}, therefore represents a small shift of about 15 cm^{-1} to lower energy and is evidence for ligand coordination. The same effect occurs for the lower energy N–O stretch in bipyO_2 complexes.[5] The magnitude of the shift (40–50 cm^{-1}) is larger indicating stronger bonding in the bipyO_2 complexes of first transition series cations. The shifts to lower energy are attributed to a decrease in the double-bond character of the N–O bonds as a result of oxygen coordination. The highest energy N–O stretching vibration of bipyO_2 all but disappears or becomes a weak shoulder in many of its metal complexes.[5] In terpyO_3 complexes, the corresponding absorption decreases considerably in intensity although the band is still well resolved. This band occurs in the complexes at about 1265 cm^{-1}, only a small shift to lower energy from the free ligand value.

Complexation also has a small but definite effect on

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the ligand N–O bending modes. In most of the complexes studied the free terpyO_3 N–O bending modes at 858 and 845 cm^{-1} shift to 850 and 840 cm^{-1}, respectively, or appear as a strong absorption at 840 cm^{-1} having a shoulder at 845 cm^{-1}. While the infrared spectrum of free terpyO_3 is complicated in the region of metal–oxygen stretches, it is worthwhile to mention that all of the terpyO_3 complexes exhibited new, weak absorptions in this region from 300 to 400 cm^{-1}. Some examples are: $Cu(terpyO_3)_2(ClO_4)_2$, 400 cm^{-1} (m); $Cu(terpyO_3)Cl_2$, 400 cm^{-1} (w); $Ni(terpyO_3)Cl_2 \cdot 0.5H_2O$, 375 and 350 cm^{-1} (w); $Co(terpyO_3)Cl_2 \cdot 0.5H_2O$, 380 and 320 cm^{-1} (w, sh); $Fe(terpyO_3)_2(ClO_4)_3 \cdot H_2O$, 395 cm^{-1} (m, b). If these are assigned as metal–oxygen vibrations, it appears that their intensities are much less than observed for the metal–oxygen stretches in bipyO_2 complexes.[5] In the latter systems such vibrations appear as medium to very strong absorptions in the 300–400-cm^{-1} region. On the other hand, the bipyO_2 complexes of some rare earth cations[20] recently investigated have smaller shifts for the N–O bending and stretching modes indicating weaker bonding than in the first transition series complexes. Corresponding to this, in the rare earth systems the assigned metal–oxygen stretches are all of medium intensity. Hence, the weakness of such absorptions in terpyO_3 complexes correlates with even weaker metal–oxygen bonding. In relation to the mono and corresponding bis complexes, there was little difference in their infrared spectra. Metal–chloride stretches for the mono complexes were difficult to observe and probably outside the range of our spectrophotometer.

There are two general observations about the infrared spectra which are important in establishing the structures of the complexes. First, the data indicate that the ClO_4^- ion is ionic, the spectra showing none of the band splittings which result from coordination. This means, for example, that in the bis complexes of Cu^{2+} and Co^{2+}, which other data indicate to be six-coordinate, all three of the oxygens of terpyO_3 are probably coordinated. Further, the spectra of terpyO_3 are essentially identical in all of the complexes studied, suggesting, but not proving, that the mode of coordination is the same.

X-Ray Diffraction Patterns.—Diffraction data for $Co(terpyO_3)Cl_2 \cdot 0.5H_2O$ and $Ni(terpyO_3)Cl_2 \cdot 0.5H_2O$ show them to be clearly isomorphous while $Cu(terpyO_3)Cl_2 \cdot 0.5H_2O$ gives a completely different set of *d* spacings and intensities. Other data to be discussed show these systems to be pseudotetrahedral. However, as is often the case with copper, its tetrahedron may be more flattened[21,22] toward a square-planar arrangement, possibly resulting in a different diffraction pattern. The orange $Mn(terpyO_3)Cl_2 \cdot 3H_2O$ complex was found to decompose in light and no satisfactory diffraction patterns were obtained for this substance.

The X-ray diffraction patterns for $Co(terpyO_3)_2(ClO_4)_2$, $Cu(terpyO_3)_2(ClO_4)_2$, and $Fe(terpyO_3)_2(ClO_4)_2 \cdot 3H_2O$ showed the complexes to be isomorphous and most likely isostructural. However, the corresponding nickel complex gave a completely different diffraction pattern for which there is no simple explanation at present. Other data show that all of the bis systems are pseudooctahedral and, in particular, that the Cu^{2+} and Fe^{2+} are rather distorted. Perhaps the lack of isomorphism of the nickel perchlorate complex compared to the others is related to less distortion in this system.

Conductivity Data.—The molar conductivities of some terpyO_3 complexes in dimethylformamide are given in Table II. The values observed for the bis complexes correspond well to those found for analogous six-coordinate complexes of pyridine N-oxide[2] and bipyO_2[4] in DMF. The values of Λ in DMF were found to range from 85 mho/mol downward for 1:1 salts, 140–170 mho/mol for 1:2 salts, and 200–260 mho/mol for 1:3 salts.[2] Therefore the conductivities in conjunction with solution spectra of the bis complexes of Co^{2+}, Ni^{2+}, and Cu^{2+} indicate them to be six-coordinate 1:2 electrolytes while $Fe(terpyO_3)_2(ClO_4)_3 \cdot H_2O$ is a six-coordinate 1:3 electrolyte. The mono-terpyO_3 complexes in Table II clearly fall into another grouping which by their values of Λ are 1:1 electrolytes in DMF. The slightly higher value of Λ for $Ni(terpyO_3)Cl_2 \cdot 0.5H_2O$ is probably due to some disproportionation to the bis or other types of decomposition. The reflectance and solution spectra of this compound are not the same. Further, Λ was observed to change the most with time for this system. It should be mentioned that conclusions of solid-state structure based on conductivity data, particularly in a strong ligand such as DMF, must be regarded as tentative although the data when used in conjunction with data from other sources can be useful.

Table II

Molar Conductivities[a] in Dimethylformamide at 25°

Complex	Λ, mho/mol	Ionic nature
$Co(terpyO_3)Cl_2 \cdot 0.5H_2O$	40	1:1
$Co(terpyO_3)_2(ClO_4)_2$	147	1:2
$Ni(terpyO_3)Cl_2 \cdot 0.5H_2O$	99	1:1
$Ni(terpyO_3)_2Cl_2 \cdot 5H_2O$	122	1:2
$Ni(terpyO_3)_2(ClO_4)_2 \cdot 2H_2O$	163	1:2
$Cu(terpyO_3)Cl_2 \cdot 0.5H_2O$	58	1:1
$Cu(terpyO_3)_2(ClO_4)_2$	167	1:2
$Fe(terpyO_3)_2(ClO_4)_3 \cdot H_2O$	244	1:3
$Fe(terpyO_3)Cl_3$	55	1:1

[a] All solutions were 0.5 m*M* and showed signs of solvolysis on standing with the formation of a white precipitate, presumably terpyO_3.

Magnetic Data.—Table III contains the magnetic data at room and liquid nitrogen temperatures for all of the terpyO_3 complexes studied. Values of μ_{eff} within the ranges normally observed[23] are found for all of the complexes except those of manganese and also the complex $Fe(terpyO_3)_2(ClO_4)_3 \cdot H_2O$. The latter compound has a moment only slightly above the spin-

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TABLE III

MAGNETIC DATA[a]

Complex	Temp, °K	$10^{-6}\chi_g$, cgsu	$10^{-6}\chi_M$, cgsu	μ_{eff}, BM
$Cu(terpyO_3)Cl_2 \cdot 0.5H_2O$	296.8	3.32	1,640	1.98
	80	13.62	6,010	1.97
$Cu(terpyO_3)_2(ClO_4)_2$	284.6	1.62	1,740	1.99
	80	6.04	5,390	1.86
$Ni(terpyO_3)Cl_2 \cdot 0.5H_2O$	285.5	13.80	6,020	3.72
	80	42.88	18,230	3.43
$Ni(terpyO_3)_2Cl_2 \cdot 5H_2O$	295.6	5.65	4,820	3.38
	80	20.94	16,780	3.29
$Ni(terpyO_3)_2(ClO_4)_2 \cdot 2H_2O$	296.5	4.91	4,630	3.33
	80	19.23	16,890	3.30
$Fe(terpyO_3)_2(ClO_4)_2 \cdot 3H_2O$	292.5	14.71	13,250	5.60
	80	55.83	49,070	5.63
$Fe(terpyO_3)Cl_3$	294.1	30.27	13,660	5.70
	80	116.52	51,910	5.75
$Fe(terpyO_3)_2(ClO_4)_3 \cdot H_2O$	297.2	16.20	15,590	6.10
	80	63.61	59,910	6.21
$Co(terpyO_3)_2(ClO_4)_2$	295.0	10.66	9,150	4.67
	80	38.26	31,790	4.53
$Co(terpyO_3)Cl_2 \cdot 0.5H_2O$	295.4	20.86	8,980	4.63
	80	73.93	31,280	4.49

[a] The diamagnetic corrections were made as outlined in ref 22 and the correction for $terpyO_3$ was taken as 162×10^{-6} cgsu.

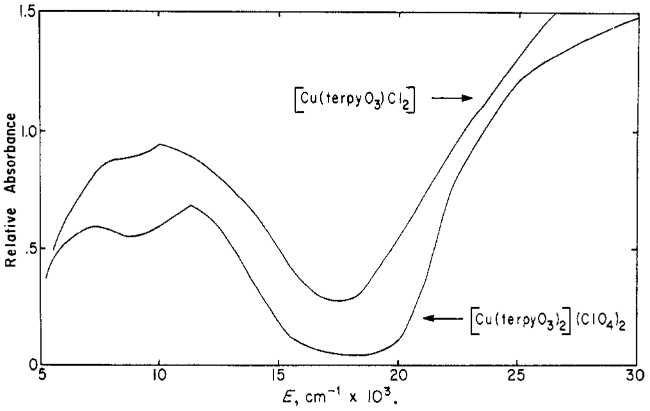

Figure 1.—Reflectance spectra of the mono and bis complexes of Co(II).

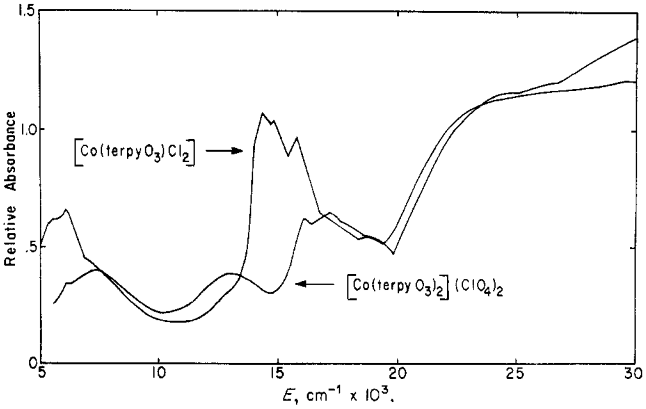

Figure 2.—Reflectance spectra of the mono and bis complexes of Ni(II).

only value of 5.92 BM expected for high-spin Fe^{3+}. A similar high moment (6.13 BM) was observed by Simpson, *et al.*,[4] for $Fe(bipyO_2)_3(ClO_4)_3 \cdot 3H_2O$ and an even higher value (6.4 BM) was observed by Madan and Bull[6] for $Fe(bipyO_2)_3(ClO_4)_3 \cdot bipyO_2$. Hence whether the elevated moments are a real property of these systems is not clear. The divalent manganese complex has an effective moment considerably in excess of that expected for high-spin d^5 and this is attributed to impurities and the very unstable nature of this complex. A similar very high value of μ_{eff} (6.34 BM) was observed for the unstable $Mn(bipyO_2)_3PtCl_4$.[4] The Mn^{3+} complex is expected to have a μ_{eff} near the spin-only value of 4.90 BM for a high-spin d^4 system. We obtained a value of ~6 BM. The high value is most likely indicative of significant amounts of Mn^{2+} impurity which need not, however, be reflected in the analytical data for this system. That the latter system is mainly Mn^{3+} is indicated by its dark color and rich-reflectance spectrum. The Mn^{2+} system is bright orange and shows, as expected, no spin-allowed transitions. The same color relationships were found for $bipyO_2$ complexes of Mn^{2+} and Mn^{3+}.[4,13]

The magnetic moment of $Cu(terpyO_3)Cl_2 \cdot 0.5H_2O$ is compatible with a structure intermediate between square planar and tetrahedral although values of μ_{eff} close to 2.0 BM are often associated[24] with copper complexes having stereochemistries more closely approximating tetrahedral. The value of μ_{eff} for $Cu(terpyO_3)_2(ClO_4)_2$ is reasonable for tetragonal copper and this is supported by its electronic spectrum (to be discussed). The low value of μ_{eff} for $Co(terpyO_3)Cl_2 \cdot 0.5H_2O$ is in the range often found for tetrahedral Co^{2+} [25] while the similar low value for the bis complex is compatible with the highly distorted octahedral system.[26] Magnetic criteria for stereochemistry are sometimes tenuous, especially for powders where susceptibility anisotropies[27,28] cannot be considered. However, there appears to be a good correlation of magnetic moment and stereochemistry for the bis- and mono-nickel complexes reported here. The magnitudes of μ_{eff} for the bis-nickel complexes are in the range normally observed for distorted octahedral Ni^{2+} complexes, especially those having six oxygens bonded to the metal.[29] On the other hand, the mono-nickel complex shows a significantly larger moment and greater temperature dependence, both expected[23] for tetrahedral Ni^{2+}.

Electronic and Mössbauer Spectra.—The reflectance spectra of several of the $terpyO_3$ complexes are shown in Figures 1–4. Solution spectra in DMF and water were also obtained; however, the reflectance spectra are presented as they are better resolved and could be determined over a larger energy range. The sharpness of some of the peaks is a feature of reflectance spectra which is sometimes observed and nothing of significance should be concluded from this. The band positions have been confirmed by both solution and mull tech-

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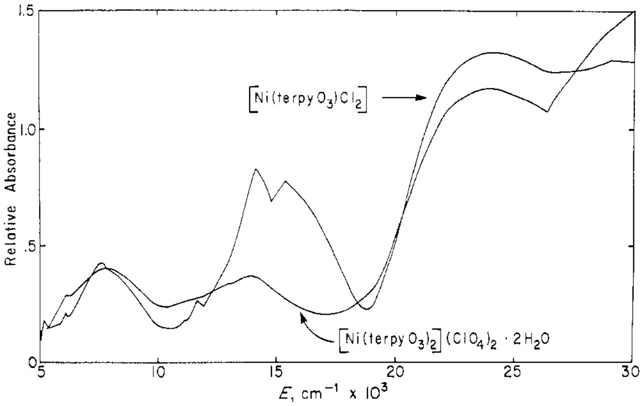

Figure 3.—Reflectance spectra of the mono and bis complexes of Cu(II).

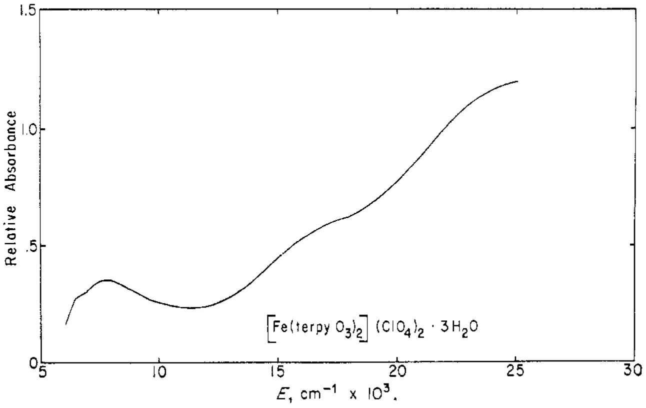

Figure 4.—Reflectance spectrum of [Fe(terpyO$_3$)$_2$](ClO$_4$)$_2$·3H$_2$O.

niques. The spectra for the bis- and mono-cobalt complexes (Figure 1) are typical of octahedral and tetrahedral Co^{2+}, respectively. The spectra in DMF are essentially the same as in the solid although the low-energy bands near 6000 cm^{-1} for Co(terpyO$_3$)Cl$_2$·0.5-H$_2$O cannot be studied using DMF. The extinction coefficients are reasonable for the systems involved with ϵ somewhat larger for the tetrahedral system. The value of 10*Dq* (Table IV) for the bis-cobalt complex is comparable to that observed by Meek, *et al.*,[30] for hexakis(dimethyl sulfoxide) and hexakis(tetramethylene sulfoxide) complexes of Co^{2+}. The *B* value of this complex is somewhat smaller than expected and this may be related to the graphical method of fitting the spectra of this system. The value of 10*Dq* for the mono complex is comparable to that of the $CoCl_4^{2-}$ ion.[14] The value of *B* is about 40 cm^{-1} smaller than observed for the latter system indicating a greater nephelauxetic effect in the terpyO$_3$ system.

The electronic spectrum of Ni(terpyO$_3$)Cl$_2$·0.5H$_2$O is very similar to that of the pseudotetrahedral (C$_6$H$_5$-AsO)$_2$NiCl$_2$.[14] Further, its derived ligand field parameters in Table IV are not significantly different from those of the foregoing phenylarsonium system. The system decomposes in DMF and water giving poorly defined spectra. The spectrum of Ni(terpyO$_3$)$_2$(ClO$_4$)$_2$·2H$_2$O and Ni(terpyO$_3$)$_2$Cl$_2$·5H$_2$O are identical and are like those usually observed for weak field, octahedral Ni^{2+}. Values of *Dq* and *B* are very close to those observed for hexakis(dimethyl sulfoxide) and hexakis(tetramethylene sulfoxide) complexes[30] of Ni^{2+} and clearly indicate the weak-field nature of terpyO$_3$. An interesting trend emerges on comparing the values of *Dq* of pyridine N-oxide, bipyO$_2$, and terpyO$_3$. The values of 10*Dq* for $Ni(C_2H_5NO)_6^{2+}$ [30] and $Ni(bipyO_2)_3^{2+}$ are 8403 and 8570 cm^{-1}, respectively. Hence, there is an increase in 10*Dq* owing to the chelate effect although not as large as observed[31] on going from $Ni(py)_6^{2+}$ (Dq = 10,150 cm^{-1}) to $Ni(bipy)_3^{2+}$ (10 Dq = 12,790 cm^{-1})[32] where three five-membered chelate rings are involved as compared to three seven-membered for the corresponding bipyO$_2$ system. In going from $Ni(bipy)_3^{2+}$ to $Ni(terpy)_2^{2+}$ (10Dq = 12,700 cm^{-1}),[33] there is essentially no change in 10*Dq* while the similar change for the N-oxide system results in a noticeable decrease in 10*Dq*. The overall decrease in 10*Dq* is probably related to the presence of seven-membered chelate rings in $Ni(terpyO_3)_2^{2+}$ although particular aspects of the geometry of the ligand may also be involved.

The spectrum of Cu(terpyO$_3$)$_2$(ClO$_4$) is essentially the same for the solid state and in solution in DMF or water although shifts to higher energy are apparent. If the system is pseudooctahedral, then the two components of the near-infrared spectrum (Figure 3) suggest a large distortion from cubic symmetry. Consideration of the geometry of the "parent" ligand terpyridine, as well as terpyO$_3$, indicates such a distortion is most likely tetragonal or trigonal. The magnitude of the splitting (~4000 cm^{-1}) and the shape of the spectrum of Cu(terpyO$_3$)$_2$(ClO$_4$)$_2$ compare with that of Cu(hfacac)$_2$(py)$_2$[34] (hfacac = hexafluoroacetylacetonate). This system is probably best assumed to be tetragonal with a strong axial field giving a splitting of about 6000 cm^{-1}.

It was difficult to determine whether the spectra of Cu(terpyO$_3$)Cl$_2$·0.5H$_2$O were the same in DMF solution and the solid. Although conductivity data indicate one chloride is coordinated in DMF, the broad, poorly resolved band centered at about 10,000 cm^{-1} is indicative of weak coordination by the solvent. Assuming that only one chloride is coordinated and that Cu(terpyO$_3$)Cl$_2$·0.5H$_2$O is four-coordinate in the solid, a stereochemistry intermediate between tetrahedral and planar is suggested[35] by the reflectance spectrum in Figure 3. The energies of the first two transitions are rather low for planar copper having predominantly oxygen coordination. On the other hand, the spectrum compares better to that of bis(N-isopropylsalicylideneamino)copper(II)[36] which has transitions at 8500, 13,500, and 21,000 cm^{-1} and has been shown to be a flattened pseudotetrahedral system. The possibility of five-coordination or a cation–anion structure such as [Cu(terpyO$_3$)$_2$][CuCl$_4$] has not been ruled

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TABLE IV

ELECTRONIC SPECTRA OF terpyO_3 COMPLEXES

Complex	Band maxima, cm^{-1} Reflectance	DMF soln[a]	Band assignment	$10Dq$, cm^{-1}	B, cm^{-1}
Co(terpyO_3)$Cl_2 \cdot 0.5H_2O$	5,800		$^4A_2 \rightarrow {}^4T1(F)$	3640	690
	6,800				
	13,200 sh				
	14,400	14,810 (270)			
	14,800		$^4A_2 \rightarrow {}^4T_1(P)$		
	15,800	16,390 (195)			
Co(terpyO_8)$_2$(ClO_4)$_2$	7,300	7,700 (31)	$^4T_1(F) \rightarrow {}^4T_2$	8030	730
	13,000	13,250 (42)	$^4T_1(F) \rightarrow {}^4A_2$		
	16,050	15,750 (123)	$^4T_1(F) \rightarrow {}^4T_1(P)$		
	17,150	17,090 (143)			
	18,000 sh	18,520 (118)			
Ni(terpyO_3)$Cl_2 \cdot 0.5H_2O$	7,700		$^3T_1(F) \rightarrow {}^3A_2$	4000	835
	14,050		$^3T_1(F) \rightarrow {}^3T_1(P)$		
	15,300				
	16,000 sh				
Ni(terpyO_3)$_2$(ClO_4)$_2 \cdot 2H_2O$	7,800	7,940 (22)	$^3A_2 \rightarrow {}^3T_2$	7800	896
		8,700 sh (13)			
	12,000 sh	12,500 sh (12)			
	13,050 sh		$^3A_2 \rightarrow {}^3T_1(F)$		
	13,800	13,790 (21)			
	23,800	22,990 (1000)	$^3A_2 \rightarrow {}^3T_1(P)$		
Fe(terpyO_3)$_2$(ClO_4)$_2 \cdot 3H_2O$	7,800		or CT	7800	
	18,200 sh		$^5T_2 \rightarrow {}^5E$		
Cu(terpyO_3)$_2$(ClO_4)$_2$	7,330	7,550 (65)	$^2E \rightarrow {}^2T_2$	9300	
	11,300	11,700 (109)			
Cu(terpyO_3)$Cl_2 \cdot 0.5H_2O$	8,000				
	9,950	10,000 (45)			
	23,500 sh				
Mn(terpyO_3)$_2$(ClO_4)$_3$	6,250				
	7,270				
	8,700 sh				
	17,950				

[a] Molar extinctions in parentheses.

out. However the mono-terpyO_3 systems of Co^{2+} and Ni^{2+} show characteristically tetrahedral spectra in the solid state, and from this point of view there is little reason to believe that the copper system is five-coordinate. The cation–anion structure also seems unlikely since the $CuCl_4^{2-}$ anion has absorption bands[35] at 8300 and 9000 cm^{-1}. One would therefore expect that the superposition of these on the bands of Cu(terpyO_3)$_2^{2+}$ would result in a very broad unresolved band. As can be seen in Figure 3, that is not the case. On the basis of the above comments, of course, neither the five-coordinate structure nor the cation–anion structure is *conclusively* eliminated, and the structure of the mono complex must be considered to be uncertain.

The electronic and Mössbauer spectra of the Fe^{3+} are typical of the high-spin d^5 configuration. Only weak electronic absorptions corresponding to spin-forbidden transitions are observed. In solution it was difficult to observe any transitions except for a sharp one at 19,400 cm^{-1} ($\epsilon \sim 47$) in the bis complex. The Mössbauer spectrum of this system consists of a small asymmetric quadrupole doublet. The values of the quadrupole splitting and isomer shift were difficult to determine owing to the poor resolution and low-percentage absorption for the bis complex, even at 80°K. This low-percentage absorption correlates with a small recoil-free fraction which can result from very weak metal–ligand bonding. The Mössbauer spectrum of Fe(terpyO_3)Cl_3 was much better resolved and consisted of an asymmetric quadrupole doublet with quadrupole splitting 0.26 mm/sec at 300°K and 0.21 mm/sec at 80°K and the corresponding isomer shifts +0.41 and +0.45 mm/sec. The latter parameters are consistent with four-, five-, or six-coordinate high-spin Fe^{3+}. The data do show conclusively that only one type of iron is present, thus strongly suggesting a mononuclear structure.

The ferrous system Fe(terpyO_3)$_2$(ClO_4)$_2 \cdot 3H_2O$ is easily distinguished from the preceding Fe^{3+} systems by its electronic (Figure 4) and Mössbauer spectra. The room-temperature isomer shift, +1.07 mm/sec, and quadrupole splitting of Fe(terpyO_3)$_2$(ClO_4)$_2 \cdot 3H_2O$, 1.77 mm/sec, are typical of six-coordinate Fe^{2+}.[37] The magnitude of the quadrupole splitting indicates distortion from a cubic electronic charge distribution. However, a similar effect was difficult to see in a reflectance spectrum owing to interference by a ligand overtone at 6000 cm^{-1}. The broad absorption between 15,000 and 18,000 cm^{-1} is believed to correspond to a charge-transfer absorption. The system is rather unstable and in DMF solution oxidized rapidly to give a conductance corresponding to a 1:3 electrolyte.

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The electronic spectra of Mn^{2+} and Mn^{3+} complexes differed significantly from each other. The divalent complex decomposed in the light path of the spectrometer, but for fast scans reflectance spectra showing only weak absorptions expected for high-spin d^5 were obtained. The Mn^{3+} system showed a rich spectrum with intense absorptions enumerated in Table IV. In a recent detailed study of the spectra[38] of octahedral Mn^{3+} complexes, the unusual low-energy bands for these systems were attributed to transitions between the components of a Jahn–Teller split ^5E_g ground state. Transitions to a similarly split $^5T_{2g}$ excited state were also observed. In the present investigation, the near-infrared transitions are observed at energies even lower than those of the studies just cited. This is attributed to the weak-field nature of terpyO$_3$ combined with a more highly distorted arrangement of the six oxygens in Mn(terpyO$_3$)$_2$(ClO$_4$)$_3$.

Conclusions

The results of this investigation show that terpyO$_3$ readily forms a series of pseudooctahedral and tetrahedral complexes. The best interpretation of the data indicates that terpyO$_3$ acts as a tridentate ligand although the evidence for this in some of the complexes, particularly Cu(terpyO$_3$)Cl$_2$ and Ni(terpyO$_3$)$_2$(ClO$_4$)$_2$·2H$_2$O, is not as conclusive. It is interesting that there is little tendency for the formation of five-coordinate complexes while the "parent" ligand terpyridine forms an extensive series of such complexes with the first transition series metals. The lack of planarity of terpyO$_3$ and its acting as a base for a "C_{3v}" pyramid may favor four-coordination. Solid-state packing effects for such a bulky ligand are also probably important but difficult to estimate in their effect on stereochemistry.

Acknowledgment.—The authors wish to thank the National Science Foundation for support of this work.

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Conformational Analysis of Coordination Compounds. III. Bis- and Tris-Bidentate Complexes Containing Five-Membered Diamine Chelate Rings

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Received September 8, 1969

Previously published experimental data concerning the energy differences between the various configurations of Co(en)$_3^{3+}$ have been reinterpreted, and it has been shown that there is very little energy difference between the D(δδδ) {=L(λλλ)} and D(δδλ) {=L(λλδ)} configurations and that both these structures are considerably preferred over the other configurations. Estimation of these energies based on conformational energies arising from van der Waals, torsional, and angle-bending energy terms has shown that the energy differences are very sensitive to the type of van der Waals equation used. The more established equations for this type of system due to Hill and Mason and Kreevoy were found to be completely inadequate in accounting for the observed energy differences. Although the Bartell nonbonded interaction equation was able to account satisfactorily for the difference in energy between the D(δδδ) and D(λλλ) configurations, it erroneously predicted that the D(δδλ) configuration was significantly more stable than D(δδδ). Empirical equations of the Hill type were developed to account for the energy differences, and these were tested by applying them to the estimation of the energy difference between the axial and equatorial orientations of the methyl group in methylcyclohexane. An energy of the right order was obtained. For *cis*-bis-ethylenediamine complexes, the *a priori* calculations showed that there is very little energy difference between the possible configurations, and, for the *trans* isomer, the chiral and *meso* configurations were found to have identical energies.

The preferred configurations for tris-ethylenediamine and related complexes have been the subject of a number of recent investigations. Corey and Bailar estimated from conformational energy calculations that, for the D distribution of chelate rings, the energy of the possible configurations increased in the order (δδδ) < (δδλ) < (δλλ) < (λλλ) with an energy difference between the D(δδδ) and D(λλλ) configurations of 1.8 kcal mol^{-1}.[1] This was in reasonably good agreement with an experimentally determined value of 1.6 kcal mol^{-1}.[2] Prior to 1968, all X-ray evidence supported this preference for the D(δδδ) or L(λλλ) configurations, as no other configuration had been found in the crystalline state.[3,4] However, more recently, Ibers and his coworkers have reported examples of each of the other configurations in pentacyanonickelate(II) and hexacyanocobaltate(III) salts of tris(ethylenediamine)chromium(III).[5]

cis-Bis-ethylenediamine complexes, in which the remaining octahedral positions are occupied by uniden-

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