This result also prompted us to question the oxidation of $OMo(S_2CNEt_2)_2$ by N_2O which was described[16] as producing N_2 and purple $Mo_2O_3(S_2CNEt_2)_4$ (amounts unspecified) in a 2-day period. Repetition of this experiment under the conditions described (but again using vacuum line techniques and a Toepler pump to collect the gas) showed that no more N_2 was produced from a $CHCl_3$[17a] solution of $OMo(S_2CNEt_2)_2$ than was produced from $CHCl_3$ alone and that no purple color was ever present in the reaction mixture. The same change from pink to yellow that was observed in the absence of oxidizing agent was also seen in the presence of N_2O.

Thus, we find no evidence for oxo transfer between $OMo(S_2CNEt_2)_2$ and $OPPh_3$ or N_2O as was reported.[16] Some of the discrepancies between our work and that of Mitchell and Scarle may be due to inadvertent aerial oxidation of $OMo(S_2CNEt_2)_2$ by these latter authors.

Conclusions. The reduction of easily prepared *cis*-dioxomolybdenum(VI) complexes (MoO_2L_2) by oxo transfer to tertiary phosphine is a convenient method of synthesis for Mo(IV) ($OMoL_2$) and/or Mo(V) ($Mo_2O_3L_4$) species. The Mo(IV) complexes are produced *only* if the interaction of $OMoL_2$ with unreacted MoO_2L_2 (eq 5) is an equilibrium because the $Mo_2O_3L_4$ complexes do not appear to be directly reducible by tertiary phosphines. Oxidation of $OMoL_2$ by oxo transfer from tertiary phosphine oxide does not occur. Kinetic and thermochemical studies, which should provide further insight into the mechanism of these oxo abstraction reactions, are currently in progress.

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Registry No. $MoO_2(acac)_2$, 21884-95-7; $MoO_2(S_2PPh_2)_2$, 31398-25-1; $MoO_2[S_2P(i\text{-}Pr)_2]_2$, 60349-60-2; $Mo_2O_3(acac)_4$, 18285-19-3; $Mo_2O_3(ox)_4$, 17979-39-4; $Mo_2O_3(cyst\text{-}OMe)_4$, 23700-02-9; $Mo_2O_3[S_2PPh_2]_4$, 59796-78-0; $Mo_2O_3[S_2P(OEt)_2]_4$, 60384-05-6; $Mo_2O_3(S_2CNEt_2)_4$, 20023-86-3; $OMo[S_2P(i\text{-}Pr)_2]_2$, 60349-61-3; $OMo(S_2PPh_2)_2$, 59796-76-8; $OMo(S_2CNEt_2)_2$, 25395-92-0; $OMo[S_2P(OEt)_2]_2$, 25395-91-9; $OMo[S_2P(OMe)_2]_2$, 59796-75-7; $(NH_4)_6Mo_7O_{24}$, 12520-87-5; $MoO_2(ox)_2$, 21884-98-0; $MoO_2(cyst\text{-}OMe)_2$, 29683-37-2; $MoO_2(S_2CNEt_2)_2$, 18078-69-8; $OPPh_3$, 791-28-6; N_2O, 10024-97-2; $CHCl_3$, 67-66-3.

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(19) The complex $OMo(S_2CNEt_2)_2$ is very stable under anaerobic conditions in CH_2Cl_2. We have observed *no* color change from pink over a 12-day period for a reaction mixture containing $OMo(S_2CNEt_2)_2$ and $OPPh_3$ in a 1:3 ratio.

Contribution from the Department of Chemistry, University of New Orleans,
New Orleans, Louisiana 70122

Substituted 1,8-Naphthyridine Complexes of Iron(II) and Iron(III)

M. A. CAVANAUGH, V. M. CAPPO, C. J. ALEXANDER, and M. L. GOOD*[1]

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The compounds $[Fe(2\text{-methyl-}1,8\text{-naphthyridine})_4](ClO_4)_2\cdot 2H_2O$, $[Fe(2,7\text{-dimethyl-}1,8\text{-naphthyridine})_3](ClO_4)_2\cdot 2H_2O$, $[Fe(2\text{-methyl-}1,8\text{-naphthyridine})_4](ClO_4)_3\cdot H_2O$, $[Fe(2,7\text{-dimethyl-}1,8\text{-naphthyridine})_4](ClO_4)_3\cdot H_2O$, $[Fe(2\text{-methyl-}1,8\text{-naphthyridine})_2Cl_2]\cdot H_2O$, and $[Fe(2,7\text{-dimethyl-}1,8\text{-naphthyridine})_2Cl_2]\cdot 3H_2O$ have been prepared and characterized by their Mössbauer, magnetic, and spectral properties. Also, the Mössbauer parameters of the previously reported $[Fe(2,7\text{-dimethyl-}1,8\text{-naphthyridine})_3](ClO_4)_2$ have been obtained. A modified synthesis of the ligands has been perfected and is reported in detail.

Introduction

Complexes of transition metals with 1,8-naphthyridine (napy) and 2,7-dimethyl-1,8-naphthyridine (2,7-dmnapy) have been extensively studied by Hendricker and co-workers. The unique eight-coordinate complexes of the first-row transition metal ions and the napy ligand have been isolated and characterized.[2] The ligand binds through the two nitrogen sites creating a four-membered chelate ring.[3] The chelate "bite" of the 1,8-naphthyridine system is ~2.2 Å[4] and satisfies the steric requirements for the abnormally high coordination number. The crystallographic structure of the eight-coordinate Fe(II) complex prepared by Hendricker and Bodner[5] revealed that the planarity of the naphthyridine ligand was maintained although one Fe–N bond distance on each ligand was lengthened to accommodate bidentate bonding from all four ligands.[4] Thus, the complex has significant distortion from high symmetry since there are four "long" and four "short" Fe–N bond lengths. The presence of this distortion has been dramatically substantiated by the observation of a very large (4.49 mm/s) quadrupole splitting in the Mössbauer spectrum of the perchlorate salt $[Fe(napy)_4](ClO_4)_2$.[6,7]

1,8-Naphthyridine complexes have also been prepared with Pd(II),[2] Ag(I),[8] alkaline earths,[9] molybdenum and tungsten carbonyls,[10] rare earth nitrates,[11] and transition metal nitrates.[12] These studies have shown that the naphthyridine moiety behaves as a monodentate ligand in some cases. The ligand has also been found as a bridging ligand in a series of nickel complexes.[13,14] The ligand has a basicity nearly equivalent to that of pyridine and it usually competes effectively with water for metal coordination sites in aqueous media although mixed ligand–aquo complexes have been isolated.[15] One unique, seven-coordinate complex, $[Hg(napy)_3(ClO_4)](ClO_4)$, has been characterized by x-ray crystallography as having three coordinated bidentate napy ligands and one perchlorate bonded to the metal through an oxygen atom.[16]

The substituted naphthyridine, 2,7-dimethyl-1,8-naphthyridine, has been found to form complexes with transition metal ions,[17] alkaline earth perchlorates,[9] and rare earth nitrates.[18] The 1:1 complex formed with dimethylgold halides exhibits fluxional behavior.[19] Several nickel complexes of the singly substituted 2-methyl-1,8-naphthyridine have been prepared where the two nitrogens are presumably bonded to two separate nickel atoms of a binuclear dimer.[14] One might also expect this compound to function as a monodentate ligand via coordination through the more basic nitrogen adjacent to the methyl group.

The occurrence of high coordination numbers, particularly for first-row transition elements, and the possibility of fluxional behavior have created significant interest in these ligands. The iron complexes have received a great deal of attention since the structural and electronic distortion and the magnetic properties can be monitored by Mössbauer spectroscopy. This is of greater than average importance since the optical spectra of such iron systems are usually not very informative because of the presence of extensive charge-transfer bands and the ESR of such systems does not generally provide unambiguous structural or electronic assignments. The iron complexes are also of interest because of their possible relationship to the iron(II) dithiocarbamates (the chelate "bite" is very similar) which have been shown to exhibit unusual magnetic and structural properties.[20]

The study reported here was undertaken to evaluate more fully the effect of the 2- or 2,7-methyl substitution on the coordination ability of the naphthyridine system. Obviously the steric stress is increased by these substitutions and the possibility of seven- or eight-coordination is probably greatly reduced. It was anticipated that some new complexes could be prepared and characterized and that perhaps some unique four-, five-, or seven-coordinate systems might be prepared.

The substituted ligands have also been used to prepare some mixed-ligand systems containing coordinated chlorides. By analogy to the reported ferrous chloride compounds containing diimine ligands[21,22] it was hoped that we might prepare a complex having bridging naphthyridine ligands and exhibiting unusual magnetic properties.

Experimental Section

Materials and Analyses. Hydrated ferric and ferrous perchlorates were purchased from G. Frederick Smith Co. and used without further purification although care was taken to be sure the materials were protected from the atmosphere. All methanol used was reagent grade, dried over molecular sieves (Davidson Type 3A) just prior to use. All other chemicals were reagent grade and used without further purification.

Elemental analyses of the new complexes were performed by Robertson Laboratory, Florham Park, N.J. In every case the analyst reported that the samples lost weight which is consistent with the assignment of waters of hydration to the species as deduced from the elemental analysis given below. The infrared spectra of the complexes also exhibited the characteristic broad water band between 3200 and 3600 cm^{-1} and a sharper band at about 1650 cm^{-1}. These water bands were of significant intensity even when extensive drybox techniques were used to prepare the KBr disks for ir analysis. Attempts were made using thermal gravimetric analysis to verify the waters of hydration as indicated by ir and elemental analysis. However, the perchlorate samples exploded before decomposition so no further data were obtained.

Synthesis. [Fe(2,7-dmnapy)$_3$](ClO$_4$)$_2$·2H$_2$O. This compound was prepared by a modification of the methods of Hendricker and Bodner.[17] Ferrous perchlorate and 2,7-dmnapy, in a molar ratio of Fe(II) to ligand of 1:3.5, were dissolved in dry ethanol and deaerated with dry nitrogen. The reaction mixture was stirred for 3 days at room temperature. The resulting bright yellow crystals were filtered, washed with dry ethanol, and dried in a vacuum desiccator over CaSO$_4$. No other products were obtained. Initial problems of mixed Fe(II)–Fe(III) products were eliminated by the exclusion of excess moisture and atmospheric oxygen.

Anal. Calcd: C, 47.03; H, 4.4; N, 10.98. Found: C, 47.25; H, 4.27; N, 11.02.

[Fe(2-mnapy)$_4$](ClO$_4$)$_2$·2H$_2$O. This yellow compound was prepared by a procedure analogous to that given above for the 2,7-dmnapy complex except that the molar ratio of Fe(II) to ligand was 1:4.2. When the ligand concentration was reduced, no new product could be isolated.

Anal. Calcd: C, 49.88; H, 4.18; N, 12.93. Found: C, 50.65; H, 4.25; N, 13.02.

[Fe(2,7-dmnapy)$_2$Cl$_2$]·3H$_2$O. FeCl$_2$·4H$_2$O was mixed with 2,7-dmnapy in methanol in a metal to ligand ratio of 1:2. The yellow solution was rotoevaporated to dryness (50 °C, 10 min), leaving the red product.

Anal. Calcd: C, 48.12; H, 5.21; N, 11.23. Found: C, 47.83; H, 4.32; N, 10.99.

[Fe(2-mnapy)$_2$Cl$_2$]·H$_2$O. FeCl$_2$·4H$_2$O was mixed with 2-mnapy in methanol in a metal to ligand ratio of 1:2. The cloudy yellow solution was rotoevaporated to dryness (50 °C, 10 min) to give a quantitative yield of red product.

Anal. Calcd: C, 49.91; H, 4.16; N, 12.94. Found: C, 49.81; H, 3.95; N, 12.63.

[Fe(2-mnapy)$_4$](ClO$_4$)$_3$·H$_2$O. This Fe(III) product was obtained using ferrous perchlorate as the starting material when reaction conditions were not well controlled with respect to oxygen and moisture. Fe(ClO$_4$)$_2$·6H$_2$O and 2-mnapy were mixed in methanol in a metal to ligand ratio of 1:4.2 and refluxed for 3 days. The pale tan product was precipitated by the addition of chloroform and washed with ether. This Fe(III) product could also be rotoevaporated out of a solution of the corresponding Fe^{II}–2-mnapy compound which had been allowed to stand for an extended period of time. The Fe(III) complex could also be prepared directly from ferric perchlorate. Fe(ClO$_4$)$_3$·6H$_2$O was dissolved in ethyl acetate and the solution dried with zeolite (Linde Type 4A molecular sieve). The 2-mnapy ligand was dissolved in chloroform and dried with zeolite.[23] After the zeolite was filtered off, the solutions were mixed with a metal to ligand ratio of 1:5.3. The light tan product formed immediately and was filtered off and washed with chloroform.

Anal. Calcd: C, 45.58; H, 3.59; N, 11.82. Found: C, 45.83; H, 4.16; N, 11.45.

[Fe(2,7-dmnapy)$_4$](ClO$_4$)$_3$·H$_2$O. Low yields of the Fe(III) complex of 2,7-dmnapy were obtained from some preparations. The results were not always reproducible. Fe(ClO$_4$)$_2$·6H$_2$O and 2,7-dmnapy in 50% ethanol were mixed in a metal to ligand ratio of 1:4 and allowed to stand for 3 days. A dark brown product was filtered off and the remaining yellow solution allowed to stand for an extended period. The cloudy solution was rotoevaporated to yield a yellow-orange product. Chloroform was added to the solid and the resulting solution rotoevaporated again, thus improving the quality of the crystals. This same Fe(III) complex was one component of the product mixture (as determined by Mossbauer spectroscopy) when ferric perchlorate was the starting material, although no pure compound could be isolated. In some experiments, a small amount of the dark brown ferric perchlorate, Fe(ClO$_4$)$_3$·6H$_2$O, was isolated from the reaction mixture using ferrous perchlorate as a starting material. In some other preparative experiments it appeared that a hydroxy species such as Fe$_2$(OH)$_2$(ClO$_4$)$_4$ was produced from the hydrolysis of Fe(III) in the perchlorate medium.[24] In both of these cases the infrared spectra indicated the total absence of the substituted napy ligand and exhibited split perchlorate bands indicative of metal–perchlorate coordination.

Anal. Calcd: C, 47.79; H, 4.18; N, 11.15. Found: C, 47.79; H, 4.55; N, 10.96.

Modified Ligand Preparation. The literature preparations[25,26] for the two substituted napy ligands were difficult to carry out in a reproducible manner. Some modifications were developed which greatly facilitated these syntheses.

A. "Sulfo-Mix" (*m*-Nitrobenzenesulfonate). Nitrobenzene (197 g, 1.6 mol) was sulfonated by running it into 20% oleum (fuming sulfuric acid, 88°g) at 20–30 °C and then heating the mixture, with stirring, to 60–70 °C over a period of ~3 h. The mixture was maintained at this temperature for an additional 6–8 h until a sample was completely soluble in water. It has taken as long as 72 h to obtain miscibility.

B. 2-Methyl-1,8-naphthyridine. A mixture of 41 g of H$_2$SO$_4$, 17.5 g of "sulfo-mix", 2.4 g (2.3 mol) of H$_3$BO$_3$, and 1.4 g (0.53 mol) of

$FeSO_4 \cdot 7H_2O$ was chilled to 0–5 °C. A 12.5-ml sample of anhydrous glycerol was added, followed by 4.3 g of 2-amino-6-methylpyridine and 22.5 ml of warmed water (50 °C), and the mixture was stirred at 135 °C for 4 h. The reaction mixture was basified with 50% NaOH (percent by weight) and filtered. The filtrate was extracted with $CHCl_3$ in a continuous-extraction apparatus and the residue was extracted with $CHCl_3$ in a Soxhlet extraction vessel. Charcoal was added to the resulting $CHCl_3$ solution which was then filtered through Celite. This final extract was dried over $MgSO_4$. The solvent was then evaporated and the residue sublimed and recrystallizated from cyclohexane. Confirmation of the ligand structure was carried out via NMR. Although precise percent yield figures were not determined for all successive preparative procedures, the yields were generally better than 25% vs. the substituted pyridine starting material.

C. 2,7-Dimethyl-1,8-naphthyridine. A 19.0-g (22.1-ml) sample of crotonaldehyde maintained at 110 °C was added to a chilled homogeneous mixture of 117 g of "sulfo-mix", 8.6 g of 2-amino-6-methylpyridine, and 45 ml of water. The crotonaldehyde was added dropwise over a 30-min period with vigorous stirring and the resulting mixture was maintained at 110 °C for another 30 min, cooled in an ice bath, and made alkaline with concentrated (50%) aqueous sodium hydroxide. The ligand was isolated as outlined above for the 2-methyl derivative. The confirmation of the ligand structure was again carried out via NMR. Again the appropriate percent yields were in the range of 25%.

Physical Methods. Mössbauer Spectra. Mössbauer parameters were obtained using an Austin Science Associates Mössbauer spectrometer operating in the constant-acceleration mode. Data were accumulated in a Nuclear Data multichannel analyzer, Series 2200, operating in the multiscaling mode. The data collected at room temperature and 4.2 K had the source and absorber at the same temperature. Data at 77 K had only the absorber cooled and were not corected for a second-order Doppler shift. Calibration of the spectrometer was accomplished by laser interferometry (via an Austin Science Associates laser system) and isomer shifts were referenced to an NBS certified iron foil standard. Data reduction was carried out by a conventional least-squares Lorentzian line shape program on a DEC PDP-10 computer.

Visible Spectra. A Cary 17 recording spectrophotometer was used to obtain solution spectra of the appropriate compounds in absolute methanol and the absorption spectra of solid complexes mounted as Nujol mulls on filter paper disks.

Infrared Spectra. Infrared spectra were determined on the samples in KBr disks on a Perkin-Elmer Model 337 or Model 357 grating spectrometer. Data below 400 cm^{-1} were obtained on a Perkin-Elmer (Hitachi) Model FIS-3 far-infrared spectrometer using samples mulled in Nujol and supported by polyethylene plates.

Magnetic Measurements. Room-temperature magnetic susceptibility measurements were carried out on Cahn 7600 Faraday magnetic susceptibility balance designed around a Cahn DTL electrobalance. Low-temperature susceptibilities were measured by Dr. D. G. Karraker at E. I. du Pont de Nemours Laboratories at the Savannah River Laboratory with a Forner-type vibrating-sample magnetometer manufactured by Princeton Applied Research Corp., operating in the field of a 12-in. electromagnet. All systems were calibrated with $Hg[Co(NCS)_4]$. Pascal's constants were used to correct the observed molar susceptibilities for the diamagnetism of the ligands. All magnetic moments were calculated using the equation $\mu = 2.84(\chi_M T)^{-1/2}$.

Results and Discussion

Mössbauer Results. The initial attempts to prepare the Fe(II) complexes of the substituted naphthyridine ligands gave products which exhibited unusual hyperfine split Mössbauer spectra which were first thought to be the results of spin relaxation effects in the Fe(II) systems (see Figure 1). This was an observation of some interest since in general hyperfine effects from slow spin relaxation in Fe(II) systems are not seen, presumably because of fast spin–lattice processes.[27] However, as indicated below for the pure compounds, the spectra in Figure 1 are the results of a mixture of Fe(II) and Fe(III) species which can be prevented by careful control of the experimental conditions. In Figure 1, the quadrupole split doublet seen at room temperature (298 K) is due to an Fe(III) impurity which has a much larger recoil-free fraction than the Fe(II) species. The middle two lines seen at 4.2 K are the larger quadrupole split doublet due to the Fe(II) species which is the major product formed. The other lines which first become noticeable at 195 K and result in a six-line hyperfine pattern at 4.2 K are due to the onset of slow spin relaxation in the Fe(III) system as the temperature is decreased. One lesson to be learned from these data is that one cannot assume that two separate iron species will exhibit similar recoil-free fractions even when the gross matrix is the same.

Table I. Mössbauer Parameters of napy Complexes and Iron Perchlorates

	IS,[a] mm/s	ΔE_Q,[a] mm/s	T, K	Ref
$[Fe(napy)_4](ClO_4)_2$	1.14	4.49	77	6
$[Fe(napy)_4](ClO_4)_2 \cdot 4H_2O$	1.35	3.27	77	6
$[Fe(napy)_4]^{2+} \cdot 4CH_3CN$ in acetonitrile	1.29	2.97	77	6
$[Fe(2,7\text{-dmnapy})_3](ClO_4)_2 \cdot 2H_2O$	1.12	1.76	77	*b*
	1.17	1.81	4.2	*b*
$[Fe(2\text{-mnapy})_4](ClO_4)_2 \cdot 2H_2O$	1.20	2.67	77	*b*
	1.22	2.74	4.2	*b*
	1.27	2.85		
$[Fe(2\text{-mnapy})_4](ClO_4)_3 \cdot H_2O$	0.46 (6-line	0.68	77	*b*
	spectrum)		4.2	*b*
$[Fe(2,7\text{-dmnapy})_4](ClO_4)_3 \cdot H_2O$	0.42 (6-line	0.60	77	*b*
	spectrum)		4.2	*b*
$[Fe(H_2O)_6](ClO_4)_3$	0.47 (6-line	0.69	77	*b*
	spectrum)		4.2	*b*
$Fe(ClO_4)_2 \cdot xH_2O$	1.14	3.38	77	*b*, 28
$[Fe(H_2O)_6](ClO_4)_3 \cdot xH_2O$	0.46		77	*b*

[a] All isomer shift values have a computational accuracy of ±0.02 mm/s and all ΔE_Q values have a computational accuracy of ±0.05 mm/s. [b] This work.

Table II. Mössbauer Parameters of Various Iron Chloride Complexes at 78 K

	IS,[a] mm/s	ΔE_Q,[a] mm/s	Ref
$Fe(2\text{-mnapy})_2Cl_2 \cdot H_2O$	1.10	3.17	*b*
$Fe(2,7\text{-dmnapy})_2Cl_2 \cdot 3H_2O$	1.12	3.38	*b*
$Fe(pyr)_4Cl_2$	1.14	3.35	29
$Fe(quin)_2Cl_2$	0.98	3.07	29
$Fe(2,9\text{-}Me_2phen)Cl_2$	0.91	2.77	29
$FeCl_2 \cdot 4H_2O$	1.25	2.94	30
$FeCl_3 \cdot 6H_2O$	0.21	0.10	28

[a] All isomer shift values have a computational accuracy of ±0.02 mm/s and all ΔE_Q values have a computational accuracy of ±0.05 mm/s. [b] This work.

The Mössbauer parameters for all of the complexes synthesized are listed in Tables I and II. The ΔE_Q values given in Table I for the perchlorate salts of the substituted napy complexes indicate that none of these new compounds contain eight-coordinate Fe(II). The quadrupole splittings are significantly reduced from the 4.49-mm/s value observed for the eight-coordinate napy complex. The parameters for $[Fe(2,7\text{-dmnapy})_3](ClO_4)_2$ are characteristic of a normal, near-octahedral, high-spin Fe(II) complex. The $[Fe(2\text{-mnapy})_4](ClO_4)_2 \cdot 2H_2O$ species exhibits an intermediate ΔE_Q value, indicating either a high coordination number or a significant distortion from octahedral symmetry. A low-temperature Mössbauer spectrum of this latter compound exhibited a four-line spectrum (Figure 2) which suggests the existence of two isomeric forms of this compound. If it is assumed that this complex has two bidentate ligands and two monodentate ligands (as suggested by the ir studies described below) the two species could be the cis and trans isomers. Space-filling models indicate that both isomers are sterically possible although the steric hindrance in the trans isomer should be minimized. This is consistent with the Mössbauer data where the smaller component exhibits the larger ΔE_Q

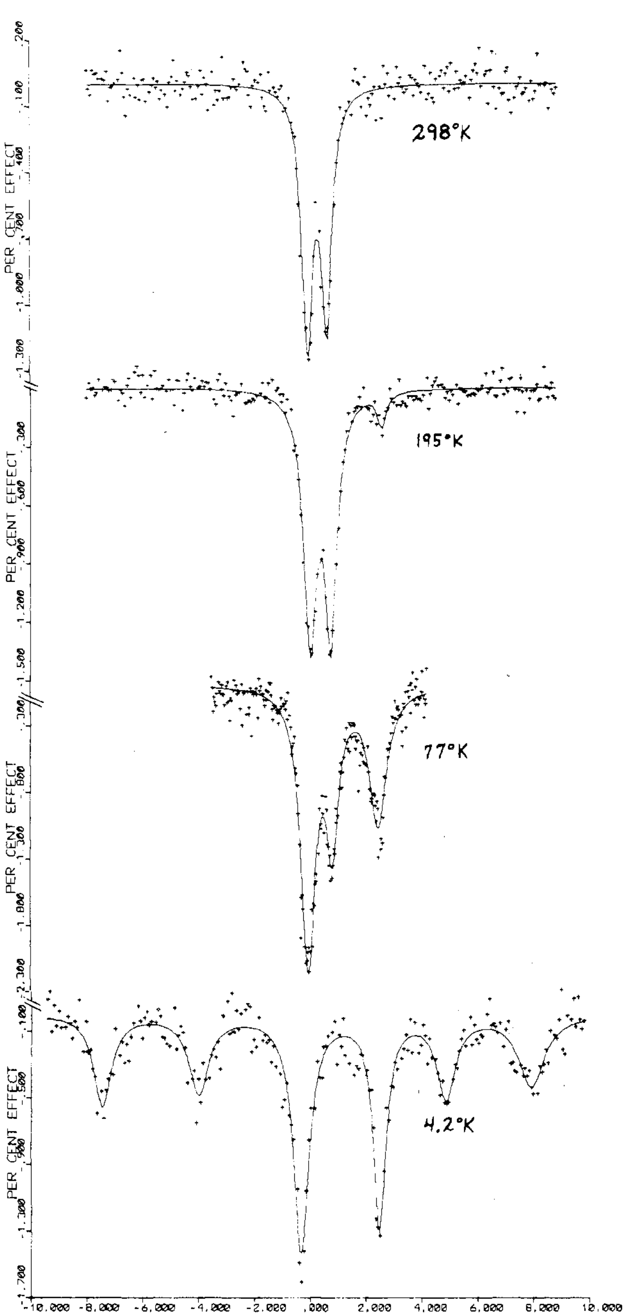

Figure 1. Temperature-dependent Mössbauer spectra of a mixture of Fe(II) and Fe(III) species in the presence of the 2,7-dimethyl-1,8-naphthyridine ligand.

value which would be expected for the cis isomer.

The iron(III)-substituted naphthyridine complexes both exhibit Mössbauer parameters which are characteristic of six-coordinate, high-spin Fe(III) systems. It is interesting that again, as in the Fe(II) case, the quadrupole splitting value for the singly substituted ligand species is larger than that observed for the doubly substituted species. The Fe(III) complexes both exhibit a magnetic hyperfine splitting pattern at 4.2 K (Figure 3). The origin of this pattern is probably slow spin relaxation caused by the isolation of the paramagnetic iron centers from one another by the large, bulky ligands. This is a common phenomenon in many bioinorganic systems such as cytochrome and hemoglobin and other Fe(III) systems which contain widely spaced iron atoms.[28,31,32] Note from Figure 3 that the hyperfine pattern is not completely resolved even at 4.2 K although the six-line spectra extend over a wide velocity range for both compounds. Effort is currently under way in our laboratory to extend the temperature range below 4.2 K and to determine the Mössbauer spectra and the magnetic properties of these Fe(III) systems at reduced temperatures. Analysis of the temperature-dependent spectra by the theoretical modeling techniques of Blume and Tjon[33] and/or Gabriel[34] should provide the numerical evaluation of the magnitude of the hyperfine interaction, V_{zz} (the electric field gradient), and η (the asymmetry parameter) for these

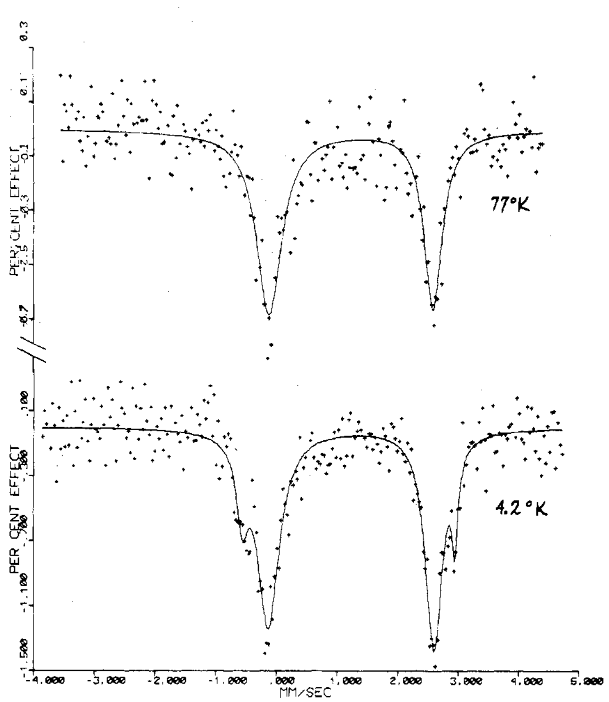

Figure 2. Temperature-dependent Mössbauer spectra of [Fe(2-mnapy)$_4$](ClO$_4$)$_2$·2H$_2$O.

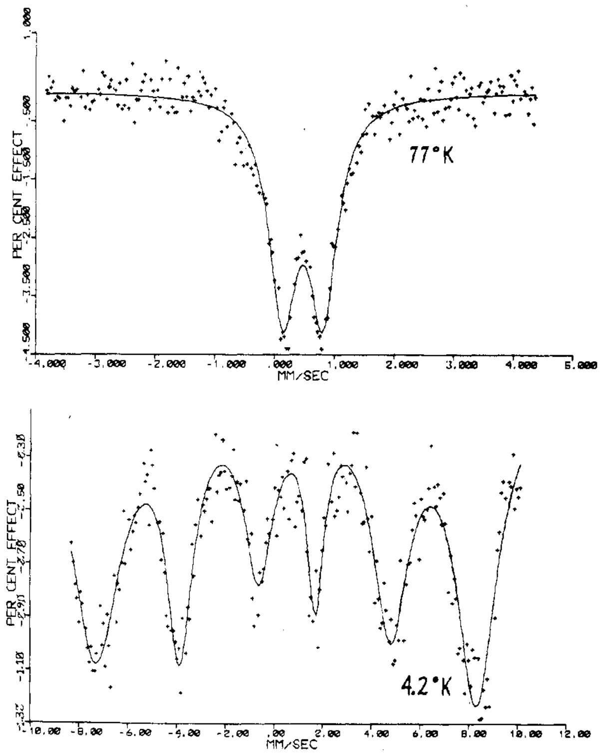

Figure 3. Temperature-dependent Mössbauer spectra of [Fe(2,7-dmnapy)$_4$](ClO$_4$)$_3$·H$_2$O.

Table III. Magnetic Moments of Substituted napy Complexes at Room Temperature

	μ_{eff},[a] μ_B
$[Fe(2,7\text{-dmnapy})_3](ClO_4)_2 \cdot 2H_2O$	5.51
$[Fe(2\text{-mnapy})_4](ClO_4)_2 \cdot 2H_2O$	5.00
$[Fe(2,7\text{-dmnapy})_2Cl_2] \cdot 3H_2O$	5.39
$[Fe(2\text{-mnapy})_2Cl_2] \cdot H_2O$	4.98
$Fe(ClO_4)_3 6H_2O$	6.16
$[Fe(2\text{-mnapy})_4](ClO_4)_3 \cdot H_2O$	4.93

[a] The values of μ_{eff} were calculated from an average of four susceptibility measurements. Reproducibility was ±0.05 μ_B.

Table IV. Electronic Spectra for napy Complexes

Compd	Spectral peak positions,[a,b] λ_{max}, nm
2-mnapy (free ligand)	312 vsp
	303 vsp
	298 vsp
	(292)
	(287)
	253 sp
$[Fe(2\text{-mnapy})_4](ClO_4)_3 \cdot H_2O$	780 w, b
	(585)
	(492)
	(362)
	318 sp
$[Fe(2,7\text{-dmnapy})_4](ClO_4)_3 \cdot H_2O$	695, 670, 630 w
	(495, 470, 440) m
	318 vsp
	310 vsp
$Fe(2\text{-mnapy})_2Cl_2$	500 b, m
	313 sp
	306 sp
	265 b
$Fe(2,7\text{-dmnapy})_2Cl_2$	510 b, (405) m
	318 sp
	308 sp
	250 b
$[Fe(2\text{-mnapy})_4](ClO_4)_2 \cdot 2H_2O$	(510) w, b
	312 vsp
	304 vsp
	300 vsp
	(293)
	(287)
	253 sp

[a] Values in parentheses are shoulders on other peaks and peak positions have been approximated. Key: v, very; sp, sharp; m, medium; b, broad. [b] All bands below 325 nm had molar absorptivities of >15 000 and can be assigned as charge-transfer bands.

complexes. It should be of significant value to compare the hyperfine parameters for the naphthyridine complexes with those of other Fe(III) systems which exhibit hyperfine spectra.

The Mössbauer isomer shift parameters for the mixed-substituted naphthyridine–chloride complexes as reported in Table II are characteristic of high-spin Fe(II) systems. The rather large quadrupole splittings of approximately 3.2 mm/s are analogous to those reported for other iron complexes having four nitrogen-bonded ligands and two trans chloride ligands.[28–30] Reiff and co-workers[29] have extensively characterized several such systems and have assigned geometries to the individual molecules based on a variety of spectroscopic and magnetic evidence. The Mössbauer parameters of species of specific geometries were then compared and correlated with the Mössbauer parameters of several compounds of known geometry. For example, $Fe(py)_4Cl_2$ is known to be a monomeric, nearly octahedral molecule[35] and $Fe(quin)_2Cl_2$ is a monomeric, nearly tetrahedral moiety.[36] A comparison with the substituted naphthyridine complexes (see Table II) would indicate essentially octahedral structures for these systems since the high value of the isomer shift would be inconsistent with tetrahedral structure.

Magnetic Studies. The room-temperature magnetic moments for the substituted naphthyridine complexes are given in Table III. All values are consistent with the Mössbauer parameters which were indicative of high-spin Fe(II) or Fe(III) species.[29] Low-temperature magnetic studies (2.5–80 K) of the chloride complexes indicate a temperature-dependent paramagnetism with a Curie temperature $\Theta = 0.4$ K. The Fe^{III}–2-mnapy species also exhibited temperature-dependent paramagnetic behavior with a negligible Curie temperature although the magnetic moment is somewhat low for a normal high-spin Fe(III) system. The very small yield of the 2,7-dmnapy species precluded the collection of reliable data for this material although initial results indicated an anomalously low moment. New samples of these two Fe(III) samples are being prepared and careful magnetic susceptibility vs. temperature measurements will be made to correlate with the temperature-dependent Mössbauer relaxation studies described above.

Electronic and Infrared Spectral Studies. The previously unreported electronic and infrared bands for this series of substituted naphthyridine complexes are given in Tables IV and V. The spectral values for the $[Fe(2,7\text{-dmnapy})_3](ClO_4)_2 \cdot 2H_2O$ compound and for the free 2,7-dmnapy ligand are not shown since they agree completely with those reported by Hendricker and Bodner.[5] In the infrared spectrum, only those bands which change substantially upon complexation are listed with their assignments. For example, the 2-mnapy modes that are not appreciably affected by coordination are

Table V. Infrared Spectral Data for napy Complexes (Band Positions in cm^{-1})

Free ligand (2-mnapy)	$[Fe(2\text{-mnapy})_4](ClO_4)_3 \cdot H_2O$	$[Fe(2,7\text{-dmnapy})_4](ClO_4)_3 \cdot H_2O$	$Fe(2\text{-mnapy})_2Cl_2$	$Fe(2,7\text{-dmnapy})_2Cl_2$	$[Fe(2\text{-mnapy})_4](ClO_4)_2 \cdot 2H_2O$	Spectral band assignments
1610	1610 m	1605 s	1620 s	1620 s	1620 s	Skel str
1550	1560 m	1535 m	1570 m	1570 m	1570 m	Skel str
1500	1490 m	1505 m	1495 s	1515 s	1480 m	Skel str
1375	1370 s	1370 s	1380 m	1385 m	1382 m	Skel str and CH sym bend, comb.
1150	1140 m	1140 m	1135 m	1150 s		Unassigned
	1080 s, b, 620 s	1085 s, 620 s			1090 s, br, 620 s	Perchlorate anion
855	845 s	860 s	845 s	860 s	850 s	CH out-of-plane bend
820	795 s	850 s	800 s	805 s	810 s	
785	780 s	785 s				
			389 m	380 m		M–Cl str, terminal Cl
292 s	290 m	353 m, 302 m	302 s	356 w, 315 w	302 m	Ring def, ligand
			242 s, 268 s	224 s, 270 s		M–Cl str, bridging Cl
	240 vw	245 w			235 w	M–N str
194 s	204 m		206 w		203 m	Ring def, ligand

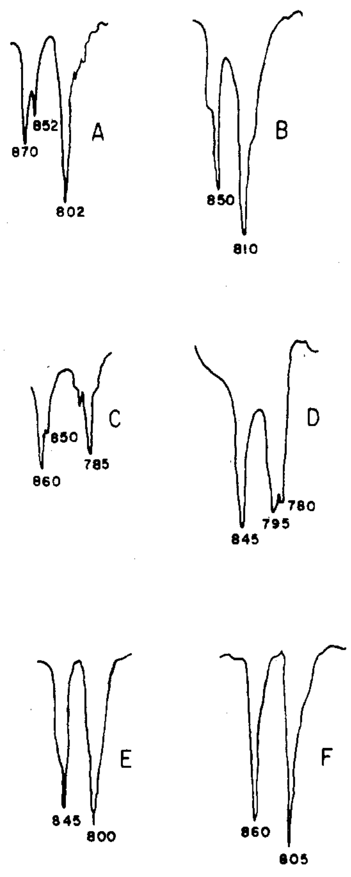

Figure 4. Comparative infrared spectra for the substituted naphthyridine complexes in the 700–900-cm^{-1} region: A, $[Fe(2,7\text{-dmnapy})_3](ClO_4)_2\cdot 2H_2O$; B, $[Fe(2\text{-mnapy})_4](ClO_4)_2\cdot 2H_2O$; C, $[Fe(2,7\text{-dmnapy})_4](ClO_4)_3\cdot H_2O$; D, $[Fe(2\text{-mnapy})_4](ClO_4)_3\cdot H_2O$; E, $Fe(2\text{-mnapy})_2Cl_2$; F, $Fe(2,7\text{-dmnapy})_2Cl_2$.

as follows (in cm^{-1}): 3040, 2990, 2915, 2850, CH stretch; 2010, 1985, 1928, out-of-plane CH bend; 1460, 1440, skeletal stretch and CH bend; 1310, 1272, 1220, CH in-plane bend; 1150, 1140, skeletal bend with $C-CH_3$ stretch; 1040, 910, unassigned; 1015, 970, skeletal stretch; 710, 665, 620, 550, 490, skeletal modes; 450, ring CH_3 bend. The infrared region between 750 and 900 cm^{-1} is apparently very sensitive to changes in the geometry and metal coordination in the complex. For example, the CH out-of-plane bends and the ring deformations are significantly affected by geometrically imposed inhibitions. These effects have been observed for copper halide complexes of 1,8-naphthyridine where the authors suggest that the spectral details in this region will be characteristic of particular N,N coordination.[37] Utilizing these empirical conclusions one can compare the infrared spectra of the substituted naphthyridines and predict certain structural properties for the individual complexes. For example, the chloride complexes are very similar in this region suggesting that they both have the same geometry. The $[Fe(2\text{-mnapy})_4](ClO_4)_2\cdot 2H_2O$ exhibits a spectrum very similar to those of the chloride complexes but the spectrum for $[Fe(2,7\text{-dmnapy})_3](ClO_4)_2\cdot 2H_2O$ is markedly different, exhibiting a splitting in the higher frequency peak (850 cm^{-1}). Details of these spectral changes are shown in Figure 4. An interpretation of these spectra which is consistent with the Mössbauer data and elemental analysis is that the substituted napy ligands are bidentate in the $[Fe(2,7\text{-dmnapy})_3](ClO_4)_2\cdot 2H_2O$ species and monodentate and bidentate in the Fe(III) complexes and in $[Fe(2\text{-mnapy})_4](ClO_4)_2\cdot 2H_2O$. The spectra for the Fe(III) species are unusual in that the ligand modes at 807 cm^{-1} (2,7-dmnapy) and 820 cm^{-1} (2-mnapy) disappear and the 778- and 785-cm^{-1} peaks, respectively, exhibit splitting upon coordination. The spectra for the chloride complexes are somewhat ambiguous indicating that the napy ligands may be both monodentate and bidentate although certainly no definitive structural assignment can be made from the infrared spectra alone. In all of the complexes studied, the perchlorate bands at 1090 and 620 cm^{-1} are typical of ionic perchlorate and exhibit no observable splitting.

The ultraviolet region of the electronic spectra of these complexes is dominated by ligand charge-transfer bands. Shoulders appear on these strong charge-transfer bands exhibited by the chloride complexes and alter the spectra enough that the chloride complexes appear red while the perchlorate salts are yellow. Although there are no discernible bands in the visible region of the Fe(II) complexes, the brown Fe(III) species exhibit weak bands at about 700 nm which may be spin-forbidden d–d transitions. Although all spectra were scanned from 2000 to 200 nm, no bands typical of tetrahedral or five-coordinate species were observed in the near-infrared region.

Bands assignable to both M–N and M–Cl vibrations are usually observed in the far-infrared region of the spectrum. In the perchlorate complexes reported here, weak bands between 235 and 245 cm^{-1} were observed. These bands are probably due to the M–N stretch of the monodentate ligands in these complexes. This assignment is consistent with the prediction of Hendricker and Bodner[5] and the observations of Hutchinson and Sunderland[38] that the M–N stretches for the ring-strained bidentate ligands are found at about 200 cm^{-1}. The increased frequency for the stronger monodentate M–N bond would be expected. The M–N stretch for the possible bidentate ligands in these complexes would be obscured by the broad ligand band at about 205 cm^{-1}.

Two strong bands in the 225–270-cm^{-1} region were observed for both of the chloride complexes, obscuring the weak 235-cm^{-1} band if it was present. The strong bands in this region can be assigned to bridging chlorides.[39] Strong bands observed at 380 cm^{-1} are typical of terminal chlorides coordinated to Fe(II). The far-infrared spectra for these chloride complexes are consistent with the assignment of similar structures to the two complexes, both having bridging and terminal chloride ligands. Thus, the overall spectral data for these chloride complexes indicate that the Fe(II) is high spin and six coordinate and that the system is probably polymeric, bridging through at least half of the chloride ligands.

Conclusion

These studies indicate that the four-membered chelate ring which is stabilized in the eight-coordinate Fe(II) complexes of the unsubstituted naphthyridine is maintained in the six-coordinate 2,7-dmnapy complex. However, the steric restrictions of the substituted ligand prevent the coordination of four 2,7-dmnapy or 2-mnapy bidentate ligands. All evidence indicates that in the 2,7-dmnapy system the bonded nitrogens are equivalent, indicating a symmetric, four-membered chelate ring. In the 2-mnapy systems, the nitrogens are not equivalent and monodentate ligation may occur, presumably through the more basic nitrogen adjacent to the methyl groups. Our data indicate that the resulting product may contain both inequivalent bidentate and monodentate coordination although the evidence is not entirely conclusive.

The products formed from the Fe(III) salts are difficult to prepare and they contain both monodentate and bidentate napy ligands. Apparently the small size of the Fe(III) cation destabilizes the four-membered chelate ring significantly. A plot of the isomer shift of these Fe(III) complexes vs. their observed 492-nm charge-transfer band is very similar to the corresponding plot for Fe(III) complexes of a series of 1,10-phenanthroline derivatives,[40] where good correlation is found between the 2,7-dmnapy and the 2-mnapy and the mono- and dimethyl substituted phenanthrolines. This would indicate that the contribution from M → L π delocalization is similar in the two cases. A more detailed study of the temperature dependence of the Mössbauer spectra and magnetic properties, particularly at very low temperatures, should provide additional information about the structure and bonding in these systems.

The mixed napy–Cl systems are interesting in that they do not exhibit the unusual magnetic properties observed for $Fe(py)_4Cl_2$ and other similar materials. The Fe(II) apparently occupies a nearly octahedral site although the infrared evidence for bridging chlorides indicates a dimeric or polymeric material. A crystallographic structural analysis of these materials would be most desirable.

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Registry No. $[Fe(2,7\text{-dmnapy})_3](ClO_4)_2$, 27628-91-7; $[Fe(2\text{-mnapy})_4](ClO_4)_2$, 60184-42-1; $[Fe(2,7\text{-dmnapy})_2Cl_2]$, 60184-51-2; $[Fe(2\text{-mnapy})_2Cl_2]$, 60184-49-8; $[Fe(2\text{-mnapy})_4](ClO_4)_3$, 60184-40-9; $[Fe(2,7\text{-dmnapy})_4](ClO_4)_3$, 60184-38-5; 2-methyl-1,8-naphthyridine, 1569-16-0; 2,7-dimethyl-1,8-naphthyridine, 14903-78-7; *m*-nitrobenzenesulfonate, 30904-40-6; 2-amino-6-methylpyridine, 1824-81-3; crotonaldehyde, 4170-30-3; $[Fe(H_2O)_6](ClO_4)_3$, 32963-81-8; $Fe(ClO_4)_2$, 13933-23-8; glycerol, 56-81-5.

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