$[Cu(bipy)_2](PF_6)_2$,[48] and $[Ag(bipy)_2](S_2O_8)$.[49] The new Cu(II) complex has been formulated as $[Cu(N\text{-}bipyO)_2](ClO_4)_2$ on the basis of the ir and conductance evidence (*vide supra*). The electronic spectral evidence is also in support of this assignment. In fact, the d-d transition appears split[48–50] and shows a pattern (Table III, Figure 4) quite similar to that of $[Cu(bipy)_2](PF_6)_2$ (λ_{max} for this complex: 590 and 700 nm).[48] $[Cu(N\text{-}bipyO)_2]^{2+}$ is, therefore, tetracoordinated and probably involves square-planar CuO_2N_2 moieties, but an overall symmetry lower than D_{4h}.[44,49,50]

Magnetic Moments. The magnetic moments of the new metal chelates are, in most cases, within the range of values reported for square-planar Cu(II) and octahedral M(II) (M = Mn, Fe, Co) compounds.[51] Only in the case of the Ni(II) chelate is the μ_{eff} (3.36 BM) slightly higher than the upper limit (3.30 BM) of the "octahedral" Ni(II) region;[51] various low-symmetry hexacoordinated cationic Ni(II) complexes (*e.g.*, complexes with pyridine *N*-oxide, dialkyl and diaryl sulfoxides, and sulfinamide) reportedly exhibit μ_{eff} values in the 3.30-3.40-BM region.[44,52] Finally, it should be mentioned that several geometrical and optical isomers and diastereoisomers of the new chelates are possible.[7,53] During the work reported here, no attempts at establishing the existence of isomeric forms of these chelates have been made. Studies in this direction are planned for the future by this laboratory.

Registry No. $[Mn(N\text{-}bipyO)_3](ClO_4)_2$, 38708-72-4; $[Fe(N\text{-}bipyO)_3](ClO_4)_2$, 38708-73-5; $[Co(N\text{-}bipyO)_3](ClO_4)_2$, 38708-74-6; $[Ni(N\text{-}bipyO)_3](ClO_4)_2$, 38708-75-7; $[Cu(N\text{-}bipyO)_2](ClO_4)_2$, 38708-76-8; $[Zn(N\text{-}bipyO)_3](ClO_4)_2$, 38708-77-9.

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(53) C. J. Hawkins, "Absolute Configuration of Metal Complexes," Interscience, New York, N. Y., 1971; A. D. Liehr, *Transition Metal Chem.*, 2, 165 (1966); R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, 7, 83 (1966), and references therein.

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Further Studies of the Coordination of Ethylenediaminedisuccinic Acid, an Isomer of Ethylenediaminetetraacetic Acid

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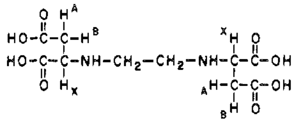
New complexes of ethylenediaminedisuccinic acid derived from (*S*)-aspartic acid, *S,S*-$EDDS^{4-}$, are reported with Rh(III) and Ni(II). The rhodium complex, $[Rh(S,S\text{-}EDDS)]^-$, is shown by analogy with the corresponding cobalt complex, $[Co(S,S\text{-}EDDS)]^-$, to contain hexadentate *S,S*-$EDDS^{4-}$ in which both aspartate moieties are in identical environments. The compound $[(CH_3)_4N]_2[Ni(S,S\text{-}EDDS)]$ has been isolated and it is proposed that the complex anion of this salt also contains hexadentate *S,S*-$EDDS^{4-}$. Infrared spectra of solutions of the Co(III), Rh(III), and Ni(II) complexes exhibit two separate bands in the 1560–1640-cm^{-1} spectral region. One is attributed to the asymmetric stretching vibration of the COO^- group of the six-membered chelate ring of *S,S*-$EDDS^{4-}$, and the other to that same vibration of the five-membered chelate ring.

Introduction

We previously reported the preparation and characterization of the cobalt(III) complex of (*S,S*)-*N,N'*-ethylenediaminedisuccinic acid[1] (hereafter *S,S*-H_4EDDS)[2] prepared from the reaction of *S,S*-$H_4EDDS \cdot H_2O$ with $Na_3[Co(CO_3)_3] \cdot 3H_2O$. In that report *S,S*-$EDDS^{4-}$ was shown to function as a stereospecific ligand for Co(III). Since that initial study, other complexes have been synthesized from *S,S*-H_4EDDS,[3] oxygen nmr studies of the Ni(II)–*S,S*-EDDS–H_2O system have been conducted,[4] the rate of CN^- replacement of *S,S*-$EDDS^{4-}$ coordinated to Ni(II) has been investigated,[5] and a single-crystal X-ray diffraction study of a hydrate of $NH_4[Co(S,S\text{-}EDDS)]$ has been performed.[6] In this paper we discuss in detail the synthesis and characterization of Ni(II)[3] and Rh(III)[3] complexes of *S,S*-$EDDS^{4-}$ as well as the synthesis of the ammonium salt of $[Co(S,S\text{-}EDDS)]^-$. For the latter



H_4EDDS

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(1) J. A. Neal and N. J. Rose, *Inorg. Chem.*, 7, 2405 (1968).

(2) Since the EDDS used in this study is prepared[1] from (*S*)-aspartic acid and $Br\text{-}CH_2\text{-}CH_2\text{-}Br$ in aqueous base, it is unlikely that racemization of the asymmetric carbon atoms of the (*S*)-aspartate moiety takes place during the synthesis. We have no evidence from fractional crystallizations of the cobalt(III) complex of EDDS or from ion-exchange chromatography of the complex that more than one species is formed. All samples of the complex prepared and isolated by whatever means exhibit the same circular dichroism spectrum. We are left to conclude that complete (100%) inversion of the asymmetric carbon atoms of the (*S*)-aspartate ion takes place in the synthesis of the ligand or that *no* inversion takes place. The latter choice seems warranted in terms of the organic chemistry involved. Thus, we designate the product of (*S*)-aspartic acid and $Br\text{-}CH_2\text{-}CH_2\text{-}Br$ as *S,S*-EDDS.

(3) J. A. Neal and N. J. Rose, Program and Abstracts, 25th Annual Northwest Regional Meeting of the American Chemical Society, Seattle, Wash., June 1970.

(4) M. W. Grant, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, 93, 6828 (1971).

(5) G. K. Pagenkopf, *J. Coord. Chem.*, in press.

(6) L. M. Woodward, M.S. Thesis, University of Washington, 1970; E. C. Lingafelter, private communication.

complex the pertinent major structural features of stereochemical significance found to date in the study of Lingafelter and Woodward[6] are discussed.

Experimental Section

With the exception of the use of a Varian HA-100 spectrometer (probe temperature 32°) and the use of solutions of approximately 0.1 g/ml contained in a fold of plastic sheets to obtain the infrared spectra in solution, the comments concerning reagents and physical measurements contained in ref 1 apply. Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium and by Galbraith Laboratories.

Preparation of *S,S*-H_4EDDS·H_2O. See ref 1 for the detailed preparation and ref 2 for comments concerning the absolute stereochemistry of *S,S*-H_4EDDS.

Preparation of NH_4[Co(*S,S*-EDDS)]·$x$$H_2O$ *via* [Co(NH_3)$_5$Br]Br_2. *S,S*-H_4EDDS·H_2O (0.620 g, 2 mmol) and [Co(NH_3)$_5$Br]Br_2 (0.767 g, 2 mmol) were dissolved in 20 ml of water. The solution was warmed on a steam bath. Ammonium hydroxide was used to adjust the acid concentration to pH 8. After 3 min the solution was acidified to pH 4.5 with acetic acid. After 3 hr on the steam bath, the solution was filtered, and ethanol (80 ml) was added slowly to the hot solution. Crystals appeared as the solution cooled. Crystals were taken from this solution for the single-crystal X-ray study and it was discovered that the hydrated water content remained more nearly constant for crystals which had "aged" in the mother liquor for several days.

Preparation of Na[Rh(*S,S*-EDDS)]. *S,S*-H_4EDDS·H_2O (0.310 g, 1 mmol) was dissolved in 1 ml of 4.00 *M* NaOH. $RhCl_3$·3H_2O (0.263 g, 1 mmol) was added and the solution was placed in a Pyrex tube which was sealed and heated to 145° for 6 hr in an oil bath. Then the tube was cooled, opened, and the solution was filtered. Addition of methanol produced a yellow precipitate which was washed with methanol and dried first in an air stream and finally at 1 Torr at 65° over P_4O_{10} to constant weight. *Anal.* Calcd for Na[Rh(*S,S*-EDDS)]·H_2O: C, 26.9; H, 3.2. Found: C, 26.4; H, 3.3.

Preparation of [(CH_3)$_4$N]$_2$[Ni(*S,S*-EDDS)]. *S,S*-H_4EDDS·H_2O (1.55 g, 5 mmol), $NiCO_3$ (0.59 g, 5 mmol), and tetramethylammonium hydroxide (0.91 g, 10 mmol, as 10% aqueous solution) were stirred into 20 ml of water and heated on a steam bath for 1 hr. During this time the solution changed to a blue color. The solution was filtered and evaporated (steam bath and air stream) to approximately 2 ml. Portions of absolute ethanol were added and evaporated until the solvent consisted of 20 ml of 95% ethanol. To this solution *n*-heptane was added until a two-phase system was achieved. This was evaporated, adding additional *n*-heptane as necessary, until a substantial crop of blue crystals had appeared. These crystals were collected and dissolved in the 48% ethanol-52% *n*-heptane azeotropic mixture. This solution was filtered and evaporated with addition of *n*-heptane as necessary. The resulting crystals were collected and dried in a stream of dry air and finally dried at 1 Torr over P_4O_{10} at 100° for 20 hr; yield 1.99 g (80%). The sample is very hygroscopic and must be carefully dried immediately prior to performing elemental analyses. *Anal.* Calcd for [(CH_3)$_4$N]$_2$[Ni(*S,S*-EDDS)]: C, 43.6; H, 7.33; N, 11.3. Found: C, 43.2; H, 7.9; N, 11.3.

Preparation of [(CH_3)$_4$N]$_2$Ni(EDTA)(H_2O)$_x$. A preparation similar to the one used for the *S,S*-EDDS complex was employed. A similar drying procedure yielded an extremely hygroscopic species definitely containing water. *Anal.* Calcd for [(CH_3)$_4$N]$_2$Ni(EDTA)(H_2O): C, 42.14; H, 7.47; N, 10.92. Calcd for [(CH_3)$_4$N]$_2$Ni(EDTA)(H_2O)$_2$: C, 40.72; H, 7.59; N, 10.55. Found: C, 41.93, 41.66; H, 7.38, 7.50; N, 10.79, 10.69.

Results and Discussion

[Co(*S,S*-EDDS]$^-$ Stereochemistry. The complex in the salt NH_4[Co(*S,S*-EDDS)]·$x$$H_2O$ was shown to be identical stereochemically with that in Na[Co(*S,S*-EDDS)]·H_2O[1] by comparing the infrared, proton magnetic resonance, electronic, and optical rotatory dispersion spectra of the two species. Thus, the major structural features obtained from the single-crystal diffraction study of the NH_4^+ salt most likely pertain to the [Co(*S,S*-EDDS)]$^-$ ion found in any salt. The major feature of the complex is that the six-membered chelate rings (hereafter the G rings) are found equatorially disposed. That is, the carboxylate oxygen atoms, O_G, of the six-membered rings are coordinated to the cobalt in the plane described by the two nitrogen atoms and the cobalt ion. This geometry, called case I in ref 1, is quite likely favored due to the expected more satisfactory "fit" of the 6-5-6-membered chelate rings in the equatorial plane *vs.* that of the 5-5-5-membered rings in [Co(EDTA)]$^-$.[7] Although the crystal structures of the species containing [Co(EDTA)]$^-$ and [Co(*S,S*-EDDS)]$^-$ are not currently at the same stage of refinement, at least three differences in the geometries of the two complexes are large enough to merit mention.[6,7] Significantly they involve the atoms associated with the equatorial rings. The most striking differences are observed in the O_G-Co-O_G angle. The six-membered chelate rings of *S,S*-EDDS^{4-} place the oxygen atoms more nearly at the apices of an imaginary equatorial square of donor atoms than do the five-membered rings of EDTA^{4-} where the O_G atoms fall significantly short of reaching the square arrangement (Table I).

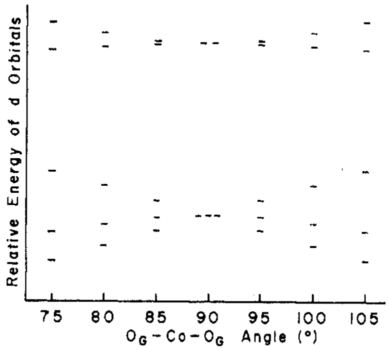

Figure 1. d-orbital energies calculated for [CoL_6]$^{3-}$ where L is assumed to be a point charge of −1.[8] Only one parameter is changed from an octahedral arrangement of L's. The L-Co-L angle for two of the cis L's is changed. This angle is called the O_G-Co-O_G angle only to show the relationship of the calculation to the complexes being discussed. A Co-L distance of 1.90 Å was used for the calculations.

Table I. Selected Structural Data of [Co(EDTA)]$^-$ and [Co(*S,S*-EDDS)]$^-$

Angle	[Co(*S,S*-EDDS)]$^-$	[Co(EDTA)]$^-$
N-Co-O_G	93.2[a]	83.2[a]
C-O_G-Co	129.4	112.9
O_G-Co-O_G	86.5	104

[a] All values are averages in degrees; data from ref 6 and 7.

This marked deviation from an octahedral array of donor atoms provoked us to wonder about the acceptability of discussing the spectra for such complexes based on an octahedral or even a tetragonal model.[1] Simple crystal field calculations performed in the manner of Companion and Komarynsky[8] tend to indicate that significant deviations from an octahedral (or tetragonal) field exist when two of the six ligand atoms, L, are displaced from an octahedral array such that one L-Co-L angle is on the order of 104° instead of 90°. Figure 1 contains the results of calculations done wherein the one L-Co-L angle is varied from 75 to 105°. As must be the case, the 90° value gives rise to the familiar octahedral field diagram. At deviations of ±15° from 90°, the energy separations within the orbitals in the lower set of three are 15-50% of the separation between the centroid of the upper two and the centroid of the lower three orbitals. Although crystal field calculations are themselves subject to uncertainty, the gross effects of deviation from an octahedral array of donors shown by these calculations strongly suggest that great care must be taken in com-

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[7] H. A. Weakliem and J. L. Hoard, *J. Amer. Chem. Soc.*, 81, 549 (1959).

[8] A. L. Companion and M. A. Komarynsky, *J. Chem. Educ.*, 41, 257 (1964).

paratively interpreting the electronic spectra of [Co(*S*,*S*-EDDS)]⁻ and [Co(EDTA)]⁻ *via* one of the commonly idealized coordination polyhedra. Thus, even after ignoring the differences between nitrogen and oxygen donor atoms, the coordination polyhedron of [Co(EDTA)]⁻ cannot be very readily considered as either an octahedron or a tetragonally distorted octahedron. Further, it is to be noted (1) that the crystal field stabilization energies for low-spin Co(III) species calculated from Figure 1 become larger (*i.e.*, more negative) the more the O_G-Co-O_G angle deviates from 90° and (2) that the energy difference between the highest filled and the lowest empty orbitals decreases as the deviation of the O_G-Co-O_G angle from 90° increases. Hence, using this crystal field model one would predict that $EDTA^{4-}$ imposes a stronger net field than *S*,*S*-$EDDS^{4-}$ and that the d-d electronic spectrum of [Co(EDTA)]⁻ might well exhibit at least one transition lower in energy than any found for [Co(*S*,*S*-EDDS)]⁻. It is significant to note that exactly the opposite conclusions are drawn when either an octahedral or tetragonal field model is presumed for the two complexes.[1] Clearly, when the geometrical restraints of the ligand lead to complexes with grossly nonideal geometries, any comparison of the species *via* their electronic spectral properties should include information obtained with models which explicitly account for the true geometrical nature of the coordination sphere.

In view of the substantial interest in correlation of circular dichroism spectra with absolute configuration[9-12] it is also appropriate to comment briefly on the absolute configuration of [Co(*S*,*S*-EDDS)]⁻. The refinement of the single-crystal X-ray data of NH_4[Co(*S*,*S*-EDDS)]·xH_2O has not, at this time, proceeded to the point where the *S* configuration of the asymmetric carbon atoms has been confirmed.[6] However, the *unambiguous placement* of the six-membered rings *demonstrated by* the X-ray study, taken with the *assumption*[2] that the original *S* configuration of the aspartic acid is preserved in the preparation of *S*,*S*-H_4EDDS, permits the absolute configuration of the complex to be specified as case I of ref 1.

[Co(*S*,*S*-EDDS)]⁻ Infrared Spectrum. The infrared spectrum of a D_2O solution of the free ligand, *S*,*S*-EDDS, is similar to that of EDTA[13,14] and is similarly dependent on acid concentration. At pD ~6.5 two bands are visible: 1615 and 1575 cm⁻¹. At pD ~9.5 the higher energy band is very weak and at pD ~11 only one band at 1575 cm⁻¹ is observed. These are all assigned to the asymmetric stretching frequencies of COO⁻ moieties without distinction between the two pairs of carboxylate groups.

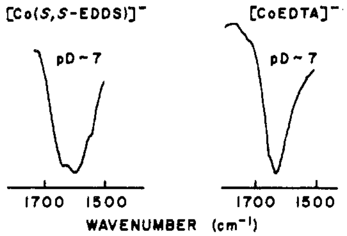

Figure 2. Portions of the infrared spectra of [Co(*S*,*S*-EDDS)]⁻ and [Co(EDTA)]⁻ in D_2O at pD ~7.

Table II. Infrared Data of D_2O Solutions (cm⁻¹)

Complex	C=O str	Chelate ring size	Ref
[Co(*S*,*S*-EDDS)]⁻	1639	5[a]	This work
	1590	6[a]	
[Co(EDTA)]⁻	1638	5	This work
cis-[Co(β-ala)$_3$]	1585	6	18
trans-[Co(β-ala)$_3$]	1585	6	18
α-[Co(gly)$_3$]	1624	5	17
[Rh(*S*,*S*-EDDS)]⁻	1635	5[a]	This work
	1580	6[a]	
[Rh(EDTA)]⁻	1630	5	This work[b]
[Ni(*S*,*S*-EDDS)]⁻	1597	5[a]	This work
	1567	6[a]	
[Ni(EDTA)]⁻	1590	5	This work[c]
[Ni(gly)$_2$]	1589	5	17

[a] Assignments proposed here. See text for discussion. [b] Another value reported for this same complex is 1641 cm⁻¹: R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 4271 (1963). Since error limits on the 1641-cm⁻¹ value are not given, we cannot tell whether the values are truly different. The maximum error in the 1630-cm⁻¹ number is estimated as ±3 cm⁻¹. [c] See text for discussion of coordination sphere.

The infrared spectrum of a D_2O solution of [Co(*S*,*S*-EDDS)]⁻ exhibits two bands thought to arise from the C-O stretch of coordinated carboxylate groups (1639, 1590 cm⁻¹).[1,15,16] Data from D_2O solutions of similar systems containing five-membered chelate rings {[Co(EDTA)]⁻, 1638 cm⁻¹; [Co(gly)$_3$], 1624 cm⁻¹;[17] [Co(α-ala)$_3$], 1612 cm⁻¹ [17]} and six-membered chelate rings {both *cis*- and *trans*-[Co(β-alanine)$_3$], 1585 cm⁻¹ [18]} support the assignment of the higher energy band to the asymmetric stretching motion of carboxylate groups contained in the five-membered chelate rings. (See Figure 2 and Table II.) Notably, the same relative position of bands is observed in spectra of five- and six-membered Cu(II) chelates of amino acids.[17] We conclude that the phenomenon may well be a general one and note that, in keeping with the observed pattern, the infrared spectrum of a new Co(III) complex[12] containing *three* five-membered aminocarboxylate chelate rings and *one* six-membered aminocarboxylate chelate ring exhibits a *strong* band at 1640 cm⁻¹ and a *weaker* band (as a shoulder) at ~1600 cm⁻¹.

Na[Rh(*S*,*S*-EDDS)]·H_2O Synthesis. Attempts to prepare [Rh(*S*,*S*-EDDS)]⁻ from $RhCl_3 \cdot 3H_2O$ and *S*,*S*-EDDS at various hydrogen ion concentrations in an aqueous medium below temperatures of 100° were not successful. However, with minor modification, the sealed-tube technique employed by Dwyer and Garvan[19] for the preparation of a Rh-EDTA complex can be effectively used to prepare the yellow monohydrate species Na[Rh(*S*,*S*-EDDS)]·H_2O (see Experimental Section). This compound is hygroscopic and dissolves readily in water to give a neutral solution. As might be expected, the salt is essentially insoluble in alcohol, acetone, and acetonitrile.

[Rh(*S*,*S*-EDDS)]⁻ Pmr and Infrared Spectra. The 100-

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(9) L. I. Katzin and I. Eliezer, *Coord. Chem. Rev.*, **7**, 331 (1972).

(10) L. J. DeHayes, M. Parris, and D. H. Busch, *Chem. Commun.*, 1398 (1971).

(11) C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, **8**, 1145 (1969).

(12) J. I. Legg, private communication.

(13) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Amer. Chem. Soc.*, **85**, 309 (1963).

(14) D. T. Sawyer and J. E. Tackett, *J. Amer. Chem. Soc.*, **85**, 314 (1963).

(15) M. L. Morris and D. H. Busch, *J. Amer. Chem. Soc.*, **78**, 5178 (1956).

(16) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963.

(17) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Amer. Chem. Soc.*, **83**, 4528 (1961).

(18) We prepared both *cis*- and *trans*-[Co(β-ala)$_3$] according to the preparation of M. B. Celap, S. R. Niketic, T. J. Janjic, and V. N. Nikolic, *Inorg. Chem.*, **6**, 2063 (1967). The infrared spectra of both isomers in D_2O solution exhibit maxima at 1585 cm⁻¹.

(19) F. P. Dwyer and F. L. Garvan, *J. Amer. Chem. Soc.*, **82**, 4823 (1960).

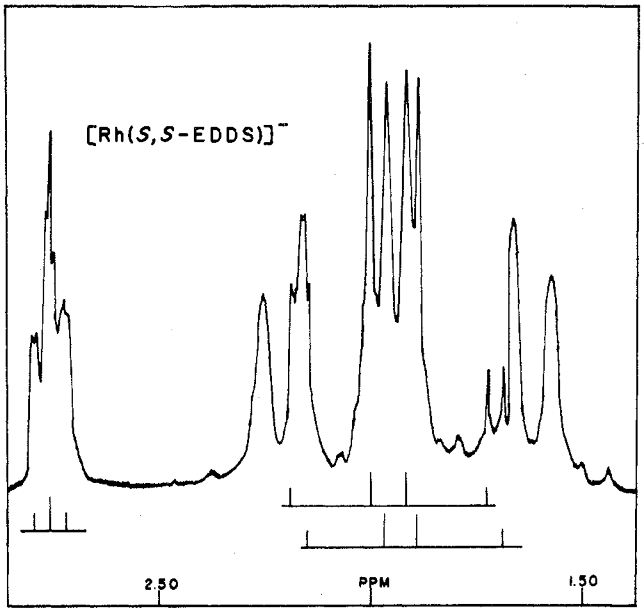

Figure 3. The 100-MHz pmr spectrum of [Rh(*S*,*S*-EDDS)]$^-$ in D_2O. Peaks assigned to the ABX pattern are shown in the line graph but no Rh coupling to the X proton is indicated in the line graph (see text).

MHz proton magnetic resonance spectrum of [Rh(*S*,*S*-EDDS)]$^-$ is fundamentally the same as that of [Co(*S*,*S*-EDDS)]$^-$ in that an ABX pattern arising from the protons of the aspartate portion of the coordinated *S*,*S*-EDDS is found superimposed on an AA′BB′ pattern arising from the ethylenic protons (Figure 3).[1] The only significant difference between the spectrum of [Co(*S*,*S*-EDDS)]$^-$ and [Rh(*S*,*S*-EDDS)]$^-$ is the fact that all the lines of the X portion of the latter spectrum are split into doublets separated by ~0.9 Hz. It is most important to note, however, that the lines attributed to the AB portion of the spectrum are sharp and exhibit *no* multiplicity beyond that expected for an unadulterated ABX pattern. Thus, it can be concluded that both aspartate moieties in the ligand are in identical environments. The most plausible explanation of the ~0.9-Hz splitting observed in the X portion of the ABX pattern is that the X protons experience coupling with the ^{103}Rh ion, the isotope of Rh which occurs in 100% natural abundance. Since ^{103}Rh has a nuclear spin of $^1/_2$, its effect on a pmr spectrum can readily be mimicked with programs meant to calculate *only* proton spectra by simply putting a "new proton" into the program, but with a vastly shifted δ and coupling constants of 0.0 to all but the proton(s) of interest. This we did by assigning the "new proton" a δ of +2.01 ppm and by allowing the coupling constant of the "new proton" to be a nonzero value only with the X proton. The results for this ABX-"Rh" system obtained from the iterative frequency-matching nmr program LAOCOON III of Bothner-By and Castellano[20] (employed in the manner of Elfring[21]) are collected in Tables III and IV. In Table III are listed the optimized values for chemical shifts and coupling constants, whereas Table IV shows the match between the observed and calculated line positions.

At this point it should also be noted that those peaks in the experimental spectrum not accounted for by the modified ABX pattern listed in Table IV are symmetrically arrayed about a point 1.86 ppm downfield from *tert*-butyl alcohol. Following the assignments for [Co(*S*,*S*-EDDS)]$^-$, these symmetrically arrayed lines constitute an AA′BB′ pattern.[1] We conclude from the pmr data that [Rh(*S*,*S*-EDDS)]$^-$, like [Co(*S*,*S*-EDDS)]$^-$, contains the ligand functioning as a hexadentate donor.

Table III. Coupling Constants and Chemical Shifts for Protons of Na[Rh(*S*,*S*-EDDS)]·H_2O in D_2O

Chem shift	Optimized value^a	Coupling const	Optimized value^c
$\delta_{\text{-CH}_2\text{-CH}_2\text{-}}$	1.86^b	J_{AX}	3.005
δ_A	1.780	J_{BX}	4.121
δ_B	1.975	J_{AB}	18.874
δ_X	2.692	J_{RhX}	0.876

^{a} All chemical shifts, δ, reported in ppm downfield from internal *tert*-butyl alcohol. Coupling constants are presented with the stated number of significant figures so that others wishing to derive the numbers listed in Table IV can do so. Admittedly there are more significant figures listed than can be verified experimentally. ^{b} Center of AA′BB′ pattern taken from experimental spectrum. ^{c} Coupling constants, J, in Hz. δ_{Rh} arbitrarily defined as 2.01 ppm upfield from internal *tert*-butyl alcohol, a chemical shift difference of 4.70 ppm from the X proton (see text).

Table IV. Comparison of Experimentally Observed ABX Pattern and That Calculated Using Parameters of Table III^a

Line	Calcd intens	Calcd position	Obsd position	Position error
1	0.574	163.69	163.70	−0.01
2	0.636	166.81	166.80	+0.01
3	3.284	182.57	182.55	+0.02
4	3.505	185.68	185.70	−0.02
5	3.241	190.29	190.30	−0.01
6	3.549	194.31	194.30	+0.01
7	0.539	209.17	209.15	+0.02
8	0.672	213.18	213.20	−0.02
9	1.093	265.80	265.80	0.00
10	1.092	266.67	266.70	−0.03
11	1.017	268.91	268.90	+0.01
12	1.017	269.79	269.80	−0.01
13	0.978	269.81	269.80	+0.01
14	0.978	270.69	270.70	−0.01
15	0.911	272.92	272.95	−0.03
16	0.912	273.80	273.75	+0.05

^{a} Line positions are listed in units of Hz downfield from *tert*-butyl alcohol.

Having established the hexadentate character of *S*,*S*-EDDS^{4-} in [Rh(*S*,*S*-EDDS)]$^-$, it is appropriate to return briefly to a discussion of the Rh-X coupling. An examination of the structure found for [Co(*S*,*S*-EDDS)]$^-$,[6] of molecular models based upon this structure and of molecular models of case II of ref 1, strongly suggests that the dihedral angle between the C-H_x and the Rh-N bond is ~160° (Figure 4). Thus, following the arguments applicable to proton-proton and platinum-proton coupling in similar systems,[22-25] the proton X will be fixed in a position for nearly maximum spin-spin coupling with rhodium. Although the 0.88 Hz found for the coupling constant is small in an absolute sense, it is reasonable considering that J_{RhH} in $[RhH(CN)_5]^{3-}$ is 13.1 Hz where hydrogen is directly bound to Rh.[26] Significant attenuation is expected in a Rh-N-C-H system compared to Rh-H where in the former system three σ bonds separate the Rh and H atoms.

As with Na[Co(*S*,*S*-EDDS)]·H_2O the infrared spectrum of

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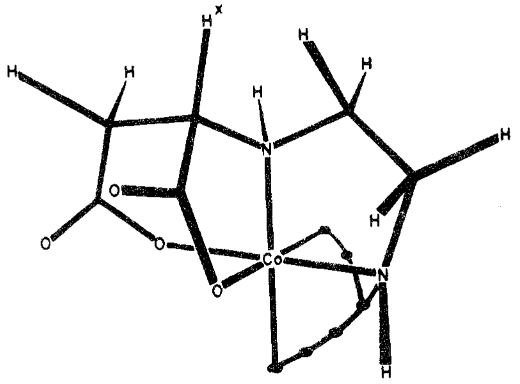

Figure 4. Stereochemical drawing of $[Co(S,S\text{-EDDS})]^-$. Only one aspartate arm and the ethylenic group are shown in full projection.

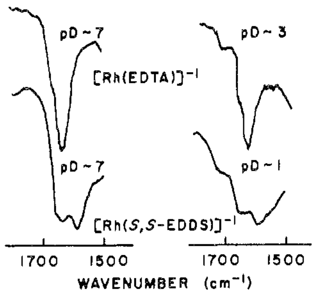

Figure 5. Portions of the infrared spectra of $[Rh(S,S\text{-EDDS})]^-$ and $[Rh(EDTA)]^-$ in D_2O.

$Na[Rh(S,S\text{-EDDS}]\cdot H_2O$ (as a Nujol mull) exhibits two strong bands which can be attributed to the asymmetric stretching vibrations of the carboxylate moieties. However, the two bands are closer in energy than for the cobalt complex: 1635 and 1600 cm^{-1} for rhodium and 1640 and 1560 cm^{-1} for cobalt.[1] Unlike the cobalt species, only a single strong band at 1380 cm^{-1} appears in the region attributed to symmetric stretching of the COO^-. At a pD of ~7 (the pD of a solution of $Na[Rh(S,S\text{-EDDS}]\cdot H_2O$ dissolved in D_2O) two maxima are again apparent in the region associated with asymmetric COO^- stretching modes (Table II). As in the case of $[Co(S,S\text{-EDDS})]^-$, the lower energy band is attributed to the COO^- of the six-membered ring, and the higher energy band to the COO^- of the five-membered rings. The distinction between $S,S\text{-EDDS}^{4-}$ and $EDTA^{4-}$ observed in the cobalt complexes is also preserved in the case of rhodium. Thus, at pD ~7, $[Rh(EDTA)]^-$ [27] exhibits a single broad band at 1630 cm^{-1}. (See Figures 2 and 5.) Clearly in neither the cobalt nor rhodium complexes are the axial and equatorial rings of $EDTA^{4-}$ different enough to impart measurable distinct bands to the asymmetric COO^- stretch.

Further information concerning the relative natures of $[Rh(S,S\text{-EDDS})]^-$ and $[Rh(EDTA)]^-$ can be obtained by examining the dependence of the infrared spectra of solutions on pD or of solid mulls on the pD of the solution from which the solid came. When the pD of a D_2O solution containing $[Rh(EDTA)]^-$ is lowered to ~3, a new band appears at 1720 cm^{-1} and a shoulder becomes visible at ~1655 cm^{-1}. The band at 1720 cm^{-1} can be attributed to a CO stretch of the COOD group.[16] The foregoing data on $[Rh(EDTA)]^-$ are consistent with Smith and Sawyer's study which indicated that only in the range pD ~4 to ~8 are all six donor atoms of EDTA bound to Rh.[27] In contrast to the $[Rh(EDTA)]^-$ species, it is observed that the $[Rh(S,S\text{-EDDS})]^-$ spectrum is essentially unchanged from pD ~9 to ~2. Clearly, this indicates an increased resistance to acid or base hydrolysis relative to $[Rh(EDTA)]^-$.

Because the coordination sphere of Rh(III) is larger[28] than that of Co(III), one would expect that $EDTA^{4-}$ would coordinately saturate Rh(III) less effectively than Co(III),[7,29] and, thus, it is not surprising that $S,S\text{-EDDS}^{4-}$ with its six-membered aminocarboxylate chelate rings exhibits improved binding *vs.* $EDTA^{4-}$. At pD ~1 a concentrated D_2O solution of $Na[Rh(S,S\text{-EDDS})]\cdot H_2O$ (0.15 g/ml) affords a precipitate, the infrared spectrum of which (as a Nujol mull) shows a band at ~1710 cm^{-1} and a decrease in the band at 1635 cm^{-1} relative to $Na[Rh(S,S\text{-EDDS})]\cdot H_2O$. As can be seen in Figure 5 a solution at pD ~1 also shows evidence of a band at or near 1710 cm^{-1}. A decrease in the intensity of the band at 1635 cm^{-1} is observed in solution at pD ≧10. Presumably, in the acidic case a predominant species present is $[Rh(S,S\text{-HEDDS})H_2O]^0$ and in the basic medium a major species might be $[Rh(S,S\text{-EDDS})(OH)]^{2-}$. In any case the data indicate that the coordination sphere of the Rh(III) is changing through the displacement of one (or more) of the carboxylate rings associated with the 1635-cm^{-1} infrared band. Assuming the band assignments given above and a stereochemistry for $[Rh(S,S\text{-EDDS})]^-$ like that of $[Co(S,S\text{-EDDS})]^-$, then it is the oxygen donor atom(s) of a five-membered chelate ring, the axial ring, which is (are) being displaced. This sort of behavior is similar to that reported with $[Co(EDTA)]^-$ where evidence is cited showing that the water molecule of $[Co(HEDTA)(H_2O)]^0$ occupies an axial coordination site.[30] Significantly, for $[Ni(HEDTA)H_2O]^-$ the water molecule is in an equatorial site.[31]

$[(CH_3)_4N]_2[Ni(S,S\text{-EDDS})]$ Synthesis. The preparations of the tetramethylammonium salts of the S,S-EDDS-Ni complex and of the EDTA-Ni complex are not nearly as straightforward as those of the complexes previously described for Rh(III) and Co(III). Both the $EDTA^{4-}$ and $S,S\text{-EDDS}^{4-}$ complexes with nickel are *very* sensitive to moisture and thus their characterization is, at once, more difficult and less definitive than those of the Rh(III) and Co(III) species. However, upon drying the $[(CH_3)_4N]_2[Ni(S,S\text{-EDDS})]$ as specified in the Experimental Section a blue powder is obtained, the elemental analysis of which suggests that little or no water is present in the sample. Thus, presuming the absence of polynuclear species, one $S,S\text{-EDDS}^{4-}$ anion is acting as a hexadentate ligand. Under the same drying conditions samples of $[(CH_3)_4N]_2[Ni(EDTA)]$ could not be desiccated and approximately one molecule of water per nickel ion appears to be present according to the elemental analyses. (See Experimental Section.)

$[Ni(S,S\text{-EDDS})]^{2-}$ Infrared and Electronic Spectra. The predominant band of the infrared spectrum of $[(CH_3)_4N]_2[Ni(S,S\text{-EDDS})]$ as a Nujol mull is rather broad and is centered at 1590 cm^{-1}. Following the preceding comments we assign this band to the asymmetric carboxylate stretching frequency.[15,16] The symmetric stretching frequency appears at 1395 cm^{-1}. Very strong, sharp bands appear at 1488 and 948 cm^{-1} which are unassigned but useful for identification. The infrared spectrum of a D_2O solution of $[(CH_3)_4N]_2[Ni(S,S\text{-EDDS})]$ shows two bands corresponding

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[27] A sample of $[Rh(EDTA)]^-$ in solution was prepared and identified according to B. B. Smith and D. T. Sawyer, *Inorg. Chem.*, 7, 2020 (1968).

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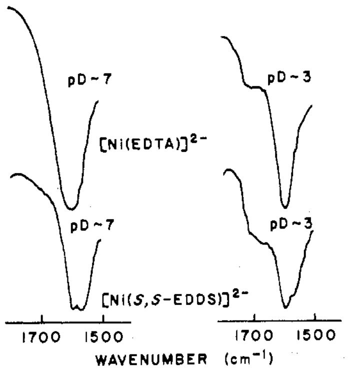

Figure 6. Portions of the infrared spectra of [Ni(*S,S*-EDDS)]$^{2-}$ and Ni^{II}(EDTA) in D_2O. See text for discussion of the coordination sphere of the EDTA complex.

to the asymmetric stretching frequencies of the carboxylate groups: 1597 and 1567 cm^{-1} (see Figure 6). Solution infrared studies of [Ni(gly)$_2$][17] and the nickel(II) nitrilotriacetate chelate[32] show that absorptions due to the asymmetric stretching modes of these five-membered chelate ring systems occur at 1589 and 1594 cm^{-1}, respectively. It is consistent therefore to assign the absorptions at 1597 and 1567 cm^{-1} for [Ni(*S,S*-EDDS)]$^-$ to the carboxylate groups of five- and six-membered chelate rings, respectively, the same ordering as for [Co(*S,S*-EDDS)]$^-$ (Table II). These assignments presume the presence (at pD's ~7) of *S,S*-EDDS^{4-} ligated in a hexadentate fashion; *i.e.*, with no uncoordinated anionic carboxylate groups present. It is difficult to establish definitively the presence or absence of the uncoordinated anionic carboxylate moiety with infrared studies since the anionic *S,S*-EDDS has a band at 1575 cm^{-1} itself, *vide infra.* However, the nmr studies of Grant, Dodgen, and Hunt[4] suggest that the predominant form of the Ni(II)-*S,S*-EDDS complex at a pH of 6.2 is the hexadentate one. Further, Pagenkopf's kinetic studies indicate that *S,S*-EDDS^{4-} is a hexadentate ligand with Ni(II) over the pH range of ~7.5-11.0.[5]

In the case of EDTA^{4-} the nmr studies indicate that significant amounts of an H_2O-EDTA-Ni(II) complex exist at pH's of 6-7.[4] It was postulated that the aquo species present is [Ni(H_2O)(EDTA)]$^{2-}$ with one carboxylate arm off the Ni(II) and unprotonated.[4] The presence of species of this type is certainly reasonable in that [Ni(EDTA)(CN)]$^{3-}$ forms readily whereas, notably, [Ni(*S,S*-EDDS)]$^{2-}$ does not form a mixed CN$^-$ complex comparable in stability to the EDTA one.[5] The infrared spectrum of the tetramethylammonium Ni(II)-EDTA complex at pD ~7 is not useful for determining the denticity of EDTA^{4-} because a free unprotonated arm of EDTA might well have an asymmetric stretching frequency close enough[13] to the bound carboxylate moieties such that they all would appear as one broad band (Figure 6). However, in more acidic solutions, it is clear from the infrared spectra that both EDTA^{4-} and *S,S*-EDDS^{4-}, to a considerable degree, now have at least one carboxylate arm uncoordinated and protonated (Figure 6, *vide infra*). As the shoulder at 1700 cm^{-1} appears, there is a concomitant decrease in the intensity of the 1567-cm^{-1} band. In the context of our previous discussion, this indicates that one of the carboxylate oxygen atoms involved in the six-membered chelate rings is the first to come out of the coordination sphere. Recalling the differences between the structures of [Co(EDTA)]$^-$,[7] [Co(*S,S*-EDDS)]$^-$,[6] and [Ni(HEDTA)H_2O]$^-$ [31] and considering the stereochemistries of EDTA^{4-} complexes,[29] we suggest that *S,S*-EDDS^{4-} can more readily serve as a hexadentate ligand for Ni(II) than can EDTA^{4-} so long as the six-membered rings of *S,S*-EDDS^{4-} provide their oxygen donor atoms to equatorial sites. Presumably, then, the geometry of [Ni(*S,S*-EDDS)]$^{2-}$ is the same as that of [Co(*S,S*-EDDS)]$^-$, with the six-membered chelate rings providing donor atoms to the equatorial positions. It follows that initial hydrolysis occurs at an equatorial position of [Ni(*S,S*-EDDS)]$^{2-}$, forming a species with the same general geometry as that of [Ni(HEDTA)H_2O]$^-$ [31] and that *S,S*-EDDS^{4-} could well be serving as a hexadentate ligand for Ni(II) in [$(CH_3)_4N$]$_2$[Ni(*S,S*-EDDS)].

Table V. Electronic Absorption Spectra for Ni(II)-*S,S*-EDDS and -EDTA Complexes (cm^{-1})

[$(CH_3)_4N$]$_2$-[Ni(*S,S*-EDDS)][a]	[$(CH_3)_4N$]$_2$-Ni(EDTA)(H_2O)[b]	[$(CH_3)_4N$]$_2$-Ni(EDTA)(H_2O)[c]
27,930	25,850	26,140
16,980	16,850	17,060
13,160[d]	12,720[d]	12,800[d]
10,910	10,020	10,090

[a] The spectral data from solid and solution samples are experimentally indistinguishable (see text). [b] Data taken from a solid mull. [c] Data taken from an aqueous solution. [d] Shoulder on the high-energy side of lowest energy band.

For [$(CH_3)_4N$][Ni(*S,S*-EDDS)] the visible spectrum remains unchanged for a sample of a solid mull, a sample in 1:1 *n*-heptane-ethanol solution and a sample in aqueous solution (see Table V). The data are consistent with the notion that the hexadentate species persists under all these conditions. The spectrum of the EDTA complex does change slightly from the solid mull to the aqueous solution (see Table V). (No spectrum of the Ni-EDTA complex in 1:1 *n*-heptane-ethanol is available for reasons of insufficient solubility.) Examination of the table reveals that in all but one case (16,980 *vs.* 17,060 cm^{-1}) the bands for the *S,S*-EDDS^{4-} complex are shifted toward higher energy relative to those of EDTA^{4-}. In view of the previous statements concerning spectral analysis it is difficult to conclude from these data which ligand imparts the stronger net field. Further, unlike the case of the Co(III) complex,[1] there is no added multiplicity found in the spectra beyond that generally seen for octahedral or pseudooctahedral Ni(II) complexes.[33]

Conclusions Concerning the Coordination of *S,S*-EDDS

1. *S,S*-EDDS^{4-} coordinates in a stereospecific hexadentate fashion to Co(III) with the carboxylate moieties in the six-membered chelate rings providing donor atoms in the equatorial positions.[1,6]

2. The [Rh(*S,S*-EDDS)]$^-$ complex contains *S,S*-EDDS^{4-} functioning as a hexadentate ligand wherein both aspartate moieties are in identical environments.

3. A reasonably large body of evidence supports the notion that *S,S*-EDDS^{4-} can readily serve as a hexadentate ligand for Ni(II) whereas the tendency for EDTA^{4-}, its isomer, to be hexadentate is significantly smaller.[4,5] This increased tendency to be a hexadentate ligand must be directly attributable to the presence of two six-membered chelate rings in *S,S*-EDDS^{4-}, as opposed to EDTA^{4-} which coordinates only *via* five-membered rings.[1,7,31]

4. The carboxylate moieties of *S,S*-EDDS^{4-}, when coordinated to Ni(II), Rh(III), and Co(III), exhibit distinctive asymmetric stretching frequencies in the infrared spectra de-

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pending upon whether they are associated with the six- or the five-membered rings. Thus, in some cases, it is possible, through infrared studies, to infer directly which rings become uncoordinated as parameters such as pH are changed.

Registry No. $NH_4[Co(S,S\text{-EDDS})]\cdot H_2O$, 38708-81-5; $[Co(NH_3)_5Br]Br_2$, 14283-12-6; $Na[Rh(S,S\text{-EDDS})]$, 38708-60-0; $RhCl_3\cdot 3H_2O$, 13569-65-8; $[(CH_3)_4N]_2[Ni(S,S\text{-EDDS})]$, 38708-61-1; $NiCO_3$, 3333-67-3; $[(CH_3)_4N]_2Ni(EDTA)(H_2O)_x$, 38708-62-2; $[Co(EDTA)]^-$, 15136-66-0; $[Rh(EDTA)]^-$, 38708-82-6.

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Encapsulation Reactions. Synthesis and Characterization of Clathro Chelates Derived from Iron(II), Dimethylglyoxime, and Boron Compounds

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Six low-spin Fe(II) clathro chelates, IV, have been isolated in very high yields from alcoholic or aqueous solutions *via* facile, single-step syntheses using iron salts, dimethylglyoxime, and either BF_3 or boric acid. When BF_3 is used, the two terminal moieties in the clathro chelate molecule (X in Figure 1) are fluorine atoms. When boric acid is employed, the X moieties are hydroxy or alkoxy groups derived from the solvent (H_2O, CH_3OH, C_2H_5OH, $i\text{-}C_3H_7OH$, or $n\text{-}C_4H_9OH$). The cage complexes exhibit high thermal stability as indicated by the fact that under conditions in the mass spectrometer (250°, 70 eV) the parent ion species corresponding to the singly ionized complex is the most predominant peak in the mass spectrum. Mossbauer spectra clearly indicate that there are distinctive differences in the iron–ligand interaction within the clathro chelates compared to low-spin Fe(II) complexes containing three symmetrical α-diimine ligands.

Introduction

A relatively few complexes containing encapsulated metal ions, clathro chelates, have been reported to date.[1-3] Even so, there are already strong reasons to believe that the study of these species will provide especially valuable information pertaining to stereochemistry,[4-6] limited-pathway intramolecular rearrangements,[7] analyses of metal ions, and ion transport phenomena.[2,8]

The synthetic routes to most of the clathro chelates are somewhat involved. Thus, examples of the tris(glyoximato) class of clathro chelates, I, were first prepared by isolating a tris(dimethylglyoximato)cobalt(III) complex and then capping this intermediate with Lewis acids such as BF_3, $SnCl_4$, or $SiCl_4$.[1,7] In another approach a bicyclic ligand flexible enough to encapsulate metal ions is synthesized and then used to prepare complexes, II, of alkali metal ions and other ions.[2] The third approach features the synthesis of a trigonally symmetric hexadentate ligand with a phosphorus bridgehead and three oxime moieties.[3] After coordination to a metal ion, this ligand is converted to a cage, III, *via* treatment with BF_3 or BF_4^-.

Recently we found a simple direct procedure for the preparation of six new clathro chelates of the tris(glyoximato) class.[1b] In this approach a metal ion salt, $DMGH_2$ (dimethylglyoxime), and BF_3 or $B(OH)_3$ are simply mixed together in alcohol. The approach was initially employed to prepare $[Co(DMG)_3(BF)_2]BF_4$, a known compound,[1a] and has subsequently been used to make the first clathro chelates of iron derived from dioximes, $[Fe(DMG)_3(BX)_2]$, IV where X is F, OH, OCH_3, OC_2H_5, $O\text{-}i\text{-}C_3H_7$, or $O\text{-}n\text{-}C_4H_9$. Herein we describe the syntheses and characterization of the six Fe(II) clathro chelates. Mass spectra and Mossbauer spectra of the complexes provide some insight into the thermal stability and the electronic nature of the complexes, respectively.

See Figure 1 for structures I-IV.

Experimental Section

The reagents used as starting materials were obtained commercially as reagent grade chemicals and were employed without further purification. Unless specified the reactions were run in flasks open to the atmosphere. The products were all dried at room temperature for at least 12 hr at ~1 Torr over Drierite.

Preparation of $[Fe(DMG)_3(BF)_2]$. A mixture of $FeCl_2\cdot 4H_2O$ (1.98 g, 0.01 mol), $DMGH_2$ (3.48 g, 0.03 mol), and 1-butanol (25 ml) was stirred for 10 min. Excess $BF_3\cdot O(C_2H_5)_2$ (10 ml) was added to the red-brown mixture; then KOH solution (2.80 g dissolved in 30 ml of 1-butanol, 0.05 mol) was added dropwise. During the addition of KOH, red crystals deposited. After cooling the mixture to room temperature, the red solid was collected and washed with small amounts of 1-butanol and petroleum spirits (yield 2.25 g, 50%). The product may be recrystallized from a hot acetonitrile–water mixture by dissolving the solid in boiling acetonitrile to which a small amount of trifluoroacetic acid (TFAA) is added and slowly adding water to the boiling solution until crystals appear. The solution is filtered and cooled to room temperature whereupon crystals deposit. Note: if the above preparation is followed omitting the

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