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Alkaloids as Ligands.
2. Synthesis and Characterization of Iron(II) Halide Complexes Containing *l*-Sparteine

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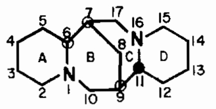
Iron(II) compounds of l-*sparteine, sp, are four-coordinate, pseudotetrahedral complexes of the type* $Fe(sp)X_2$, *where X is Cl, Br, or I. The infrared spectra suggest that sp adopts an all-chair conformation in these complexes. Furthermore, the infrared spectra show four bands below 600* cm^{-1}, *two of which are halide sensitive. These absorptions have been assigned to iron–ligand stretching modes. X-ray powder patterns of* $Fe(sp)Cl_2$ *and* $Fe(sp)Br_2$ *are identical to the analogous pseudotetrahedral cobalt(II) compounds. These iron compounds have room temperature magnetic moments close to 5.3* μ_B *and display a characteristic low-intensity absorption near 4000* cm^{-1} *which has been assigned to the* $^5E \rightarrow {}^5T_2$ *ligand-field transition. Mössbauer effect spectral results indicate the quadrupole interaction is approximately 2.9 mm/s. The chemical isomer shift increases from 1.03 to 1.25 to 1.29 mm/s (relative to α-iron foil) for the chloride, bromide, and iodide complexes respectively. The latter two values are among the highest observed for tetrahedral iron(II) complexes.*

Introduction

Recent studies [1–7] have established that sparteine (sp, 1) a tetracyclic tertiary diamine of the lupine alkaloid family, chelates divalent metal ions to form pseudotetrahedral complexes of the type $M(sp)X_2$. With the possible exception of $Co(sp)(NCSe)_2$ [1], sp adopts an all-chair conformation in these complexes (2). Such complexes of divalent calcium ion with sp are thought [8] to be responsible for the pharmacological effectiveness of sp as a muscle stimulant. The steric inequivalence of the nitrogen donor atoms of sp leads to a number of interesting spectroscopic and structural phenomena. Thus, the large splittings of ν_2 and ν_3 ligand-field absorptions in the $Co(sp)X_2$ complexes [1, 2] are believed to arise from this inequivalence as evidenced by two distinctly different Co–N bond lengths in $Co(sp)Cl_2$ [6]. Because of this interesting coordination behavior we undertook the synthesis and characterization of several iron(II) halide complexes of sp. Prior to this work only a single reference describing some iron(III) compounds containing sp was available [2]. Herein we report on the structural and electronic properties of three Fe(II) complexes with sparteine.



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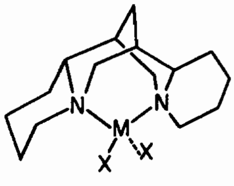

(2)

Experimental

Materials

l-Sparteine free base was obtained from Sigma Chemical Co. and used without further purification. $FeBr_2$ and FeI_2 were freshly prepared from iron powder and halogen in anhydrous methanol which had been previously distilled from Mg and stored over molecular sieves. All operations were carried out in a nitrogen-filled glove box.

Fe(sp)Cl₂

Dichlorosparteinatoiron(II) was prepared by adding a stoichiometric amount of sp to a methanol solution of anhydrous $FeCl_2$. A small amount of green material which initially precipitated was discarded and the solution volume reduced to one-third under reduced pressure. A white powder separated, was washed with diethyl ether, and dried *in vacuo* at room temperature. *Anal.* Calcd for $FeC_{15}H_{26}N_2$-

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Cl_2: Fe, 15.46; C, 49.89; H, 7.26; N, 7.76; Cl, 19.63. Found: Fe, 15.52; C, 49.89; H, 7.19; N, 7.71; Cl, 19.43.

Fe(sp)Br₂

Dibromosparteinatoiron(II) was prepared in a similar manner from anhydrous $FeBr_2$. The crude greenish-white product was conveniently recrystallized from anhydrous methanol to yield a white crystalline material which was dried *in vacuo* at room temperature. *Anal.* Calcd for $FeC_{15}H_{26}N_2Br_2$: Fe, 12.41; C, 40.03; H, 5.82; N, 6.22; Br, 35.51; Found: Fe, 12.33; C, 39.98; H, 5.86; N, 6.19; Br, 35.90.

Fe(sp)I₂

Diiodosparteinatoiron(II) was prepared in a similar manner from anhydrous FeI_2. Repeated crystallizations from methanol gave a light green product which was dried *in vacuo* at room temperature. *Anal.* Calcd for $FeC_{15}H_{26}N_2I_2$: Fe, 10.15; C, 32.76; H, 4.76; N, 5.09. Found: Fe, 9.82; C, 33.23; H, 4.89; N, 5.51.

Analytical Methods and Physical Measurements

Iron was determined by the 1,10-phenanthroline method. Halide was determined by Volhard titration. C, H, and N elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Magnetic susceptibilities were determined by using a standard Gouy balanced calibrated with $HgCo(NCS)_4$. Diamagnetic corrections were taken from tables of Pascal's constants [9]. Electronic and infrared spectra were recorded on Cary 14 and Perkin Elmer 180 spectrophotometers by using either nujol or Kel F-90 mulls. Mössbauer spectra were obtained by using an Austin Science Associates Mössbauer spectrometer calibrated with natural α-Fe foil. The source was $^{57}Co(Cu)$ and was held at room temperature for all measurements. X-ray powder photographs were obtained by using the Straumanis technique with Ni-filtered Cu Kα radiation. The d-spacings are estimated accurate to ± 0.09 Å.

Results and Discussion

The iron complexes prepared in this report are very air and moisture sensitive. Great care must be exercised to ensure that all solvents are water free. We observed that the amount of insoluble green material which formed upon addition of sp to iron halide was greatly influenced by the amount of water in the solvent methanol. If these white compounds are placed in air they decompose to a reddish brown material in a short time. $Fe(sp)I_2$ is also quite sensitive to light. We observed that samples of $Fe(sp)I_2$ sealed in brown bottles were unchanged after several days whereas samples sealed in clear bottles were discolored after this time.

TABLE I. X-ray d-Spacings and Relative Intensities.[a]

$Co(sp)Cl_2$	$Fe(sp)Cl_2$	$Co(sp)Br_2$	$Fe(sp)Br_2$
8.26 s	8.27 s	8.04 s	8.18 s
7.25 w	7.24 w	6.93 w	6.58 w
6.72 w	6.70 w	6.73 w	6.77 w
6.50 w		6.54 w	6.58 w
6.43 w	6.42 w	6.16 m	6.21 w
6.20 m	6.20 m	5.38 m	5.38 s
5.42 s	5.40 s	4.45 m	4.49 m
4.48 m	4.39 m	4.05 m	4.04 m
4.00 m	4.05 m	3.81 m	3.83 vs
3.92 m	3.96 m	3.43 w	3.50 w
3.50 w	3.51 w	3.26 m	3.26 m
3.27 w	3.26 w	3.10 w	3.13 w
3.15 w	3.15 w	3.02 w	
3.01 w	3.09 w	2.80 m	2.76 vw
	2.79 w		2.70 w
2.51 w	2.50 w		2.46 w
2.40 w	2.46 w		2.28 vw
	2.28 vw	2.24 w	2.23 vw
	2.09 vw		

[a] CuKα radiation. Data given in Å. Abbreviations: v = very; s = strong; m = moderate; w = weak.

In order to determine if the $Fe(sp)X_2$ compounds were isostructural with the $Co(sp)X_2$ compounds we obtained the X-ray powder patterns of the chloride and bromide complexes of both cobalt and iron. Table I contains a listing of these d-spacings and relative intensities. Although there are small differences between the chloride and bromide patterns, the patterns for $Fe(sp)Cl_2$ and $Fe(sp)Br_2$ are superimposible upon those of their cobalt analogs. Because $Co(sp)Cl_2$ has been shown by a recent single-crystal X-ray study [6] to have structure 2 we assume that $Fe(sp)Cl_2$, $Co(sp)Br_2$, and $Fe(sp)Br_2$ have the same structure. We encountered great difficulty in obtaining an X-ray powder pattern for $Fe(sp)I_2$ because decomposition of this compound to a red material occurred in the X-ray beam. None-the-less, evidence which follows leads us to believe that $Fe(sp)I_2$ is structurally similar to its Cl and Br analogs.

Magnetic Susceptibility Data

Magnetic susceptibility data for these complexes are given in Table II. The values are the average of data obtained on two different preparations. Both the magnitude and temperature independence of μ_{eff} for these complexes is in the range expected for high-spin pseudotetrahedral iron(II) complexes [10]. Moreover, the absence of temperature dependence for μ_{eff} indicates that impurities of six-coordinate and dimeric iron(II) complexes, if present, contribute a negligible amount to the total susceptibility.

TABLE II. Magnetic Susceptibility Data.

Compound	χ_M^c, cgsu	T, °K	χ'_M, cgsu	μ_{eff}, μ_B
$Fe(sp)Cl_2$	−195	300.1	11790	5.32
		78.0	45030	5.30
$Fe(sp)Br_2$	−206	295.6	11750	5.27
		78.0	44550	5.27
$Fe(sp)I_2$	−222	294.0	11770	5.26
		78.0	44350	5.26

TABLE III. Metal–Ligand Infrared Absorption Bands (cm^{-1}).

Compound	ν_{M-N}	ν_{M-X}	Ref.
$Fe(sp)Cl_2$	488, 390	325, 295	this work
$Co(sp)Cl_2$	493, 392	266, 255	this work
$Cu(sp)Cl_2$	468, 438	288, 272	5
$Cu(sp)Cl_2$	468, 436	297, 274	3
$Zn(sp)Cl_2$	460, 438	330, 305	5
$Fe(sp)Br_2$	488, 390	286, 240	this work
$Co(sp)Br_2$	492, 406	215, 201	this work
$Cu(sp)Br_2$	468, 436	230, 210	5
$Zn(sp)Br_2$	460, 435	230, 210	5
$Fe(sp)I_2$	487, 428	242	this work

Infrared Spectral Data

Infrared spectra of the iron(II) halide complexes of sp are very similar to those observed for other pseudotetrahedral divalent metal complexes of sp [1–7]. We observe both the absence of trans-bands as expected for chelated sp and the shifts of two δ bands in the 800–700 cm^{-1} region [1]. These two δ bands are characteristic of C–H deformation modes and their shift to lower wavenumber is diagnostic of coordinated sp [1]. In sp these deformation modes occur at 786 and 737 cm^{-1}. For $Fe(sp)Cl_2$ these bands shift to 770 and 725 cm^{-1}, respectively. $Fe(sp)Br_2$ and $Fe(sp)I_2$ show similar shifts to 764, 730 and 762, 724 cm^{-1}, respectively. In addition, the ratio of the areas of these bands is approximately 0.3 as observed for the $Co(sp)(NCX)_2$ complexes [1]. Of particular interest is the assignment of metal–ligand stretching absorptions below 600 cm^{-1}. In general, four absorptions are observed in the low-frequency region of the spectra of $M(sp)X_2$ complexes [1, 3, 5]. These absorptions are assigned to ν_{M-X} in the region below 350 cm^{-1}. A brief summary of these data is given in Table III which also contains our assignments for the $Fe(sp)X_2$ complexes. In a series, for a given metal, the two highest wavenumber bands are insensitive to the halide whereas the two lower wavenumber bands shift to lower energy as the atomic weight of the halide increases. The $\nu(MBr)/\nu(MCl)$ ratios in Table III are in the range 0.70 to 0.80 as expected [11]. Positions and assignments are, moreover, in general agreement with those of similar tertiary amine metal halide complexes [12]. We also observe small shifts of several bands below 300 cm^{-1} which are assigned to sparteine structural deformation modes.

TABLE IV. Ligand-Field Absorption Bands.

Compound	ν, cm^{-1}	Assignment
$Fe(sp)Cl_2$	4200	
	4350	$^5E \rightarrow {}^5T_2$
	4650	
	5200	sp combination
$Fe(sp)Br_2$	4000	$^5E \rightarrow {}^5T_2$
	5200	sp combination
$Fe(sp)I_2$	13750	$^5E \rightarrow {}^3T$
	32500	L → M CT

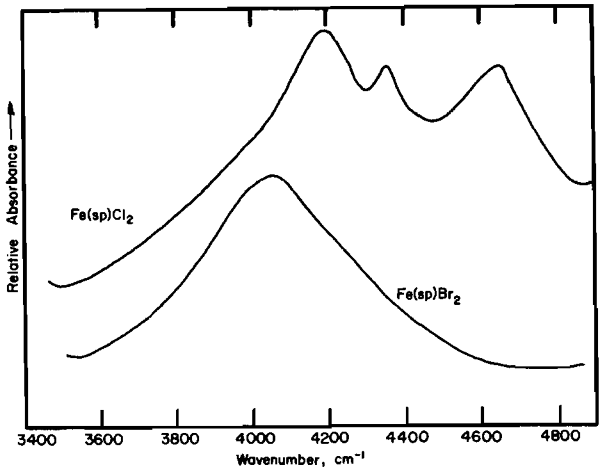

Figure 1. The room temperature fluorocarbon mull electronic absorption spectrum of $Fe(sp)Cl_2$ anf $Fe(sp)Br_2$.

Ligand-Field Spectral Data

Tetrahedral iron(II) complexes are predicted on the basis of crystal-field theory to possess a single electronic absorption band in the near infrared at 4000 to 5000 cm^{-1} which may be assigned to the $^5E \rightarrow {}^5T_2$ transition. Low-symmetry ligand-field components are expected to remove both ground and excited term orbital degeneracy thereby introducing structure in this absorption. We observe a weak absorption near 4000 cm^{-1} in mull spectra of $Fe(sp)Cl_2$ and $Fe(sp)Br_2$. The spectra of these complexes are shown in Figure 1. Band positions and assignments are given in Table IV. Because sp itself has rather intense ($\epsilon \sim 10$) combination bands in this spectral region, the exact positions of the more intense ligand-field bands must be considered tentative. Although we do observe three bands at 4200, 4350, and 4650 cm^{-1} for $Fe(sp)Cl_2$ only a single broad band near 4000 cm^{-1} is found for the bromide

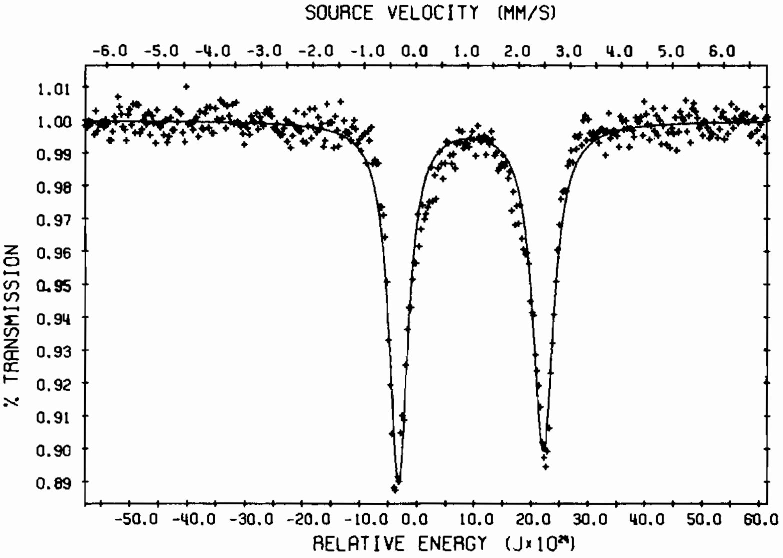

Figure 2. Mössbauer effect spectrum of $Fe(sp)Cl_2$ at 78 °K.

TABLE V. Mössbauer Spectral Parameters.[a]

Compound	T, K	ΔE_Q	δ	Γ_1	Γ_2
$Fe(sp)Cl_2$	RT	2.80	1.02	0.47	0.50
	78	2.83	1.03	0.44	0.49
$Fe(sp)Br_2$	RT	2.88	1.22	0.41	0.47
	78	2.90	1.25	0.41	0.46
$Fe(sp)I_2$	RT	effet not observed			
	78	2.98	1.29	0.43	0.47

[a] Data given in mm/s relative to natural α-Fe foil.

complex. We have attempted to observe this band in $Fe(sp)I_2$ by using concentrated CsI pressed pellets in the region 3000–4200 cm^{-1} but have been frustrated by the ease with which the iodide complex decomposes when placed in the spectrophotometer beam. For all three of the complexes we observe a sparteine vibration at 5200 cm^{-1}. The chloride and bromide complexes exhibit no absorption bands from *ca.* 5500 to 30000 cm^{-1} whereas the iodide complex shows a weak absorption at 13750 cm^{-1} and a strong absorption at 32500 cm^{-1}. We believe that the lower of these two absorptions may be assigned to a spin-forbidden transition of the type $^5E \rightarrow {}^3\Gamma$ while the 32500 cm^{-1} band is of charge-transfer origin. Low-lying charge-transfer bands are often observed for iodide complexes and are assumed to arise from the metal-ion induced polarization of the iodide valence electrons.

Mössbauer Spectral Data

The Mössbauer effect spectral parameters obtained on polycrystalline samples at room and liquid nitrogen temperatures are given in Table V. The 78K spectrum of $Fe(sp)Cl_2$ is shown in Figure 2. The magnitude of the quadrupole splitting in these three compounds is similar to that in other distorted tetrahedral Fe(II) complexes of the $Fe(II)N_2(halide)_2$ chromophoric type (*i.e.*, for $Fe(di\text{-}2\text{-}pyridylamine)_2Cl_2$, ΔE_Q = 2.71 mm/s and for $Fe(quinoline)_2Cl_2$, ΔE_Q = 2.72 mm/s) [13, 14]. In addition, the isomer shifts increase in the order Cl < Br < I as previously observed for $[Fe(II)(halide)_4]^{2-}$ complexes [15]. However, pseudotetrahedral Fe(II) complexes are usually characterized by isomer shifts in the range 0.8 to 1.1 mm/s [13, 14, 16]. The isomer shifts of $Fe(sp)Br_2$ and $Fe(sp)I_2$ are clearly outside the accepted range for four-coordinate tetrahedral Fe(II) complexes. The X-ray isomorphism of $Fe(sp)Br_2$ with its pseudotetrahedral Co(II) analog demonstrates the four-coordinate structure of this compound. It is possible to ascribe these large isomer shifts to the coordination behavior of the sparteine ligand. The two tertiary nitrogen donor atoms of sp have been shown by pK_a measurements [1] and single-crystal X-ray studies [6] to be inequivalent. Kuroda and Mason [6] found two different Co–N bond lengths for $Co(sp)Cl_2$ (Co–N(16) = 2.040(7) Å and Co–N(1) = 2.068(8) Å) and attributed this difference to the steric inequivalence of the A and D rings of sp. Furthermore, an analysis of the electronic spectra of the $Co(sp)X_2$ complexes by using C_{2v} model calculations has shown [1] that the symmetry of the ligand field in these complexes is considerably less than C_{2v}.

In addition to the quadrupole doublet with parameters listed in Table V, a small doublet is observed as shoulders in the spectra of the $Fe(sp)X_2$ complexes. This minor doublet has an isomer shift approximately equal to the major doublet but in all cases the splitting is slightly less than the major doublet. It is possible that this minor component is a configurational isomer of the Fe(sp)X_2 complexes reported here. As a consequence of this miner component, the line widths given in Table V are somewhat broader than expected.

Acknowledgment

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