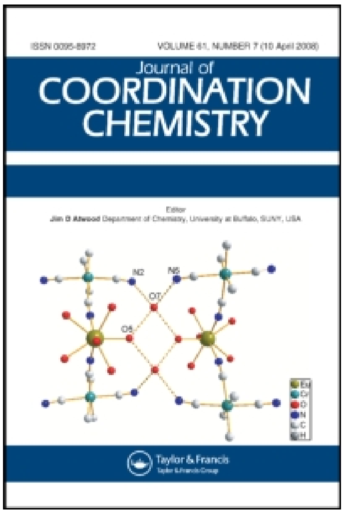

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SYNTHESIS AND CHARACTERIZATION OF (-)-SPARTEINE METAL SALT COMPLEXES

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SYNTHESIS AND CHARACTERIZATION OF (—)-SPARTEINE METAL SALT COMPLEXES

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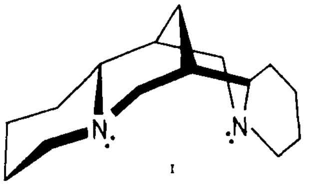
The syntheses of nineteen transition metal salt complexes of (–)-sparteine and the copper bromide complex of (–)-β-iso-sparteine are reported. All form 1:1 salt:sparteine complexes, which are soluble in organic solvents and decompose in water. Far infrared spectroscopy and the metal isotope technique were used to detect and assign metal-halide and metal-nitrogen absorption frequencies. The metal halide absorptions occur in the region from 353 to 140 cm^{-1}, and the metal-nitrogen absorptions from 468 to 181 cm^{-1}. Observed trends are discussed on the basis of changes in metal size, ionic charge, and halogens. Comparisons are drawn between these values and those for similar compounds where available.

INTRODUCTION

The natural alkaloid (–)-sparteine, $C_{15}H_{26}N_2$, has been known for over 125 years,[2] and has since been investigated mainly from the pharmaceutical point of interest.[3] It is currently marketed as an oxytocic under the tradenames *Spartocin* (Ayerst) and *Tocasamine* (Trent). Its chemistry, stereoisomers and structure were reported by Carmack in 1955.[4] Although the nitrogens are located in perfect position for chelate formation[7c] (see I), until recently only circumstantial evidence was available for possible metal complex formation. Such evidence came either through qualitative tests (see EXPERIMENTAL), or through solution studies.[5] In no case were the complexes characterized, ligand bands discussed and assigned. We reported the first isolation and characterization of a metal complex,[1a,6] and since then several other workers have shown an interest in these complexes.[7] We now report the synthesis, characterization and far infrared analysis of twenty different transition metal complexes of the alkaloid.



I

EXPERIMENTAL

Reagents

To prevent decomposition the sparteine oil was isolated as follows just prior to reaction with metal salts: Commercial sparteine sulfate pentahydrate, $C_{15}H_{26}N_2 \cdot 5H_2O$ (K&K Laboratories, Inc. or Pfaltz & Bauer, Inc.) is taken up in water and treated with an eight-fold excess of KOH through dropwise addition. The mixture is stirred for 15–20 minutes during which time the initially formed K_2SO_4 redissolves and the sparteine oil droplets appear. The oil is extracted with five 10-ml ether washings, dried over anhydrous $MgSO_4$, and the solvent stripped off. An essentially quantitative yield of the clear, colorless thick oil is obtained.

Most salts were used as obtained commercially without further purification. The isotopes ^{68}ZnO (95–99%), ^{64}ZnO (99%), ^{62}Ni (95–99%), and ^{58}Ni (98–99%), were purchased from Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830. The zinc isotopes were converted quantitatively to the chlorides by reacting with a 50-fold excess of HCl and careful heating to dryness. The nickel metal isotopes were similarly converted to the chlorides. $ZnBr_2$ and ZnI_2 were prepared quantitatively by a

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similar procedure from ZnO using HBr and HI, respectively.

Synthesis of Complexes

Table I summarizes some of the physical data for the complexes prepared for this study. Anhydrous metal halides were obtained either commercially, by oven drying, and/or through reaction with triethylortho (or methyl) formate. The metal halides were taken up in anhydrous alcohol and refluxed in alcohol sparteine solution.[1c] All complexes were prepared on the two to three millimole scale, except the metal isotope systems, which were prepared on the ½ to ¾ millimole scale.

The cobalt iodide reaction must be performed in the dark since the salt is photosensitive. For the nickel compounds we observed the formation of two complexes for each halide. Thus during reflux the chloro complex turns intense green, then yields purple crystals; the bromo system changes from dark blue to a rich purple color; and the iodo solution goes from deep maroon to brown. Both the green and the purple chloro complexes were isolated. The structure and bonding of these complexes are being investigated.

Tetrahalo complexes were predicted from the existence of complexes such as nicotine insecticide, $C_{10}H_{14}N_2H_2 \cdot CuCl_4$,[12] and synthesized by a procedure adapted from Broome, Ralston, and Thornton.[13] The gold complex was prepared by first drying aurous chloride in ethanol/triethylorthoformate during which time the yellow aurous salt disproportionates to red gold(III) chloride.

Infrared Spectra

Near infrared spectra (4000 – 670 cm^{-1}) were obtained on a Perkin-Elmer Model 137 Sodium Chloride Spectrophotometer (Infracord) using KBr pellets or Nujol mulls. The far infrared spectra were recorded on a Perkin-Elmer Infrared Spectrophotometer Model 283[21] (400 – 200 cm^{-1}), and in part in Prof. Kazuo Nakamoto's laboratory at Marquette University on a Hitachi Perkin-Elmer FIS-3 Infrared Spectrophotometer (410 – 33 cm^{-1}). In both cases the samples were prepared as Nujol mulls held between polyethylene plates. With the reference beam exposed to a polyethylene plate the spectra were obtained at scanning speeds from 1 to 2 cm^{-1}/min. The sample chamber was purged with high-purity dry nitrogen or air. Calibrations were

TABLE I
Metal complexes of sparteine[9]

Complex	Color	M.P., °C	% Calculated				% Found				Ref.
			C	H	N	Halide	C	H	N	Halide	
$Sp \cdot CoCl_2$	blue	288	49.46	7.19	7.69	19.47	49.72	7.13	7.93	19.32	8
$Sp \cdot CoBr_2$	blue	306	39.76	5.78	6.18	35.72	39.81	5.60	6.43	37.4	10
$Sp \cdot CoI_2$	blue	294 dec.	32.93	4.79	5.12	46.38	31.33	4.53	4.84	46.9	
$Sp \cdot NiCl_2$	purple	305	49.50	7.20	7.70	19.48	48.93	6.83	7.71	19.67	11
$Sp \cdot NiCl_2$	green	190 dec.	49.50	7.20	7.70	19.48	49.89	7.37	7.91	18.56	
$Sp \cdot NiBr_2$	purple	307	39.78	5.79	6.18	35.29	39.56	5.54	6.13	35.9	
$Sp \cdot NiI_2$	brown	304	32.94	4.79	5.12	46.41	33.07	4.89	4.83	47.18	
$Sp \cdot CuCl_2$	green	160	48.84	7.12	7.60	19.22	48.64	6.87	7.89	18.81	1c,2
$Sp \cdot CuBr_2$	brown	154	39.36	5.73	6.12	34.92	38.51	5.72	6.07	34.8	
β-isoSp · $CuCl_2$	yellow-green	155	48.84	7.12	7.60	19.22	49.01	7.28	7.47	18.21	1c
β-isoSp · $CuBr_2$	burnt orange	154									
α-isoSp · $CuCl_2$	blue-green	200	48.84	7.12	7.60	19.22	48.23	7.19	7.69	19.18	1c
$SpH_2 \cdot CuCl_4$	brown	129	40.78	6.40	6.36	32.10	39.28	6.66	6.07	30.71	14
$SpH_2 \cdot CuBr_4$	purple	152	29.01	4.55	4.52	51.59	28.65	4.82	4.37	49.79	
$Sp \cdot AuCl_3$	orange	125	33.51	4.87	5.21	19.78	31.64	4.67	5.08	19.6	2,15
$Sp \cdot ZnCl_2$	white	278	48.62	7.07	7.53	19.13	48.90	7.18	7.62	18.94	11
$Sp \cdot ZnBr_2$	white	297	39.20	5.70	6.09	34.77	38.94	5.60	6.02	35.09	
$Sp \cdot ZnI_2$	white	>300	32.55	4.73	5.06	45.85	32.44	4.67	5.02	45.56	16
$Sp \cdot CdCl_2$	white	262	43.13	6.27	6.71	16.98	43.14	6.28	6.68	16.87	17
$Sp \cdot CdBr_2$	white	261	35.56	5.17	5.53	31.55	34.40	4.72	5.38	30.3	
$Sp \cdot CdI_2$	white	280	30.00	4.36	4.66	42.26	30.30	4.49	4.66	42.53	18
$Sp \cdot HgCl_2$	white	132	35.61	5.18	5.54	14.02	35.44	5.13	5.54		2,19,20
$Sp \cdot HgBr_2$	yellow	143	30.29	4.41	4.71	26.87	32.92	4.43	4.71		
$Sp \cdot HgI_2$	white	157	26.14	3.80	4.06	36.82	26.07	3.79	4.02		

performed using polystyrene and water vapor. Band frequencies are reproducible to ± 0.5 cm^{-1}.

RESULTS AND DISCUSSION

All compounds synthesized here were isolated as stable crystalline materials. In a few cases the syntheses required special maneuvers, but generally they may be prepared and recrystallized using routine conditions and simple organic media. It is essential in most cases that the medium be anhydrous. The usual procedure for drying solvents was used and hydrated metal salts were dehydrated using triethyl- or trimethylorthoformate.

The near infrared spectra for all complexes were recorded. A striking observation is the similarity of infrared features between ligand and complex as well as between complexes. The few observed changes have been discussed elsewhere,[1c,7f] and will not be considered here. $MX_4^{=}$ complexes do, however, show some major variations which will be considered separately.

Of key interest in our work was the nature of the metal-ligand interaction, which we chose to study using far infrared spectroscopy. Table II shows the far infrared data for zinc(II), cadmium(II), and mercury(II) halide complexes of sparteine. The metal-ligand absorptions are expected to fall into the following order from high to low frequencies:[22] antisymmetric M–X stretch, symmetric M–X stretch, antisymmetric M–N stretch, symmetric M–N stretch, N–M–N bend, X–M–N bend, and X–M–X bend. Both antisymmetric and symmetric metal-halide stretch modes are easily detected by their marked intensity, pronounced frequency shifts upon halogen substitution, and the small but definite shifts upon metal isotope substitution.[23] Thus the lighter $^{64}ZnCl_2\cdot$sp complex records the higher frequencies of 331, 315, and 303 cm^{-1}, while the heavier $^{68}ZnCl_2\cdot$sp complex causes the lower frequency absorptions of 329, 313, and 301 cm^{-1}.

TABLE II
Far infrared frequencies, isotopic shifts, and band assignments for sparteine and its Zn^{++}, Cd^{++}, and Hg^{++} halide complexes, cm^{-1}.

	400		300		200		100	
Assignment:		M-X ν_a ν_s		M-N ν_a	ν_s δ(N-M-N)	δ(X-M-N) δ(X-M-X)		
Sparteine	392 383	$\underset{w}{347}$ 300	274	$\underset{w}{224}$ $\underset{w}{205}$				
Sp·^{64}ZnCl$_2$	$\underset{w}{382}$ 352	$\underset{s}{\underline{331}}$ $\underset{s}{315}$ $\underset{s}{\underline{303}}$	288 268	209	183 $\underset{w}{158}$	142 $\underset{sh}{120}$ $\underset{s}{\underline{115}}$ $\underset{s}{\underline{104}}$	$\underset{w}{96}$	
Sp·^{68}ZnCl$_2$	$\underset{w}{382}$ 352	$\underset{s}{\underline{329}}$ $\underset{s}{313}$ $\underset{s}{\underline{301}}$	288 268	207	181 $\underset{w}{158}$	141 $\underset{sh}{119}$ $\underset{s}{\underline{114}}$ $\underset{s}{\underline{104}}$	$\underset{w}{96}$	
Δν		3.0 2.0 2.0		2.0	2.0 0	1.0 1.0 1.0	0	
Sp·ZnBr$_2$	$\underset{w}{384}$	350 $\underset{w}{337}$ 325 $\underset{sh}{319}$	285 269 266	$\underset{s}{\underline{244}}$ $\underset{s}{\underline{218}}$ $\underset{sh}{210}$	184 $\underset{w}{154}$	133 102	$\underset{s}{\underline{87}}$ $\underset{s}{\underline{85}}$ $\underset{s}{\underline{76}}$ 55	43 36
Sp·ZnI$_2$	398 358	$\underset{w}{335}$ 326 301	285	242 $\underset{s}{\underline{216}}$ $\underset{s}{204}$	$\underset{s}{\underline{191}}$ $\underset{w}{177}$	$\underset{w}{137}$	$\underset{s}{\underline{73}}$	
Sp·CdCl$_2$	$\underset{w}{387}$ $\underset{w}{378}$	348 $\underset{w}{320}$ 310	$\underset{s}{\underline{296}}$ $\underset{s}{\underline{279}}$		161	137 101	$\underline{78}$	
Sp·CdBr$_2$	$\underset{w}{382}$ $\underset{w}{373}$	347 316 311	292 276 260	$\underline{217}$	$\underline{188}$ 163	143 138 $\underset{w}{109}$	82 $\underset{s}{\underline{67}}$ $\underset{s}{\underline{64}}$ $\underset{s}{\underline{58}}$	44 40
Sp·CdI$_2$	383 374	346 316 311	276 259		$\underline{192}$ 181 $\underline{158}$	110	$\underset{s}{\underline{59}}$ $\underset{s}{\underline{57}}$ $\underset{s}{\underline{51}}$	44 35
Sp·HgCl$_2$	388 379	347 318	$\underset{s}{\underline{289}}$ $\underset{s}{\underline{270}}$		$\underset{w}{158}$	137	$\underline{83}$ $\underline{72}$	
Sp·HgBr$_2$	377 368	340 311 304	273 256		$\underset{s}{\underline{196}}$			
HgBr$_2$				$\underset{s}{\underline{249}}$		146 139	$\underline{74}$	
Sp·HgI$_2$	383 375	344 314 307	274 257		$\underline{164}$	$\underline{140}$ 138	$\underline{71}$ $\underline{63}$	46

ν_a = antisymmetric stretch
ν_s = symmetric stretch
M–X bands are underlined
δ = bending mode
w = weak band
s = strong band
$\Delta\nu = \nu_{^{64}Zn} - {}^{68}Zn$

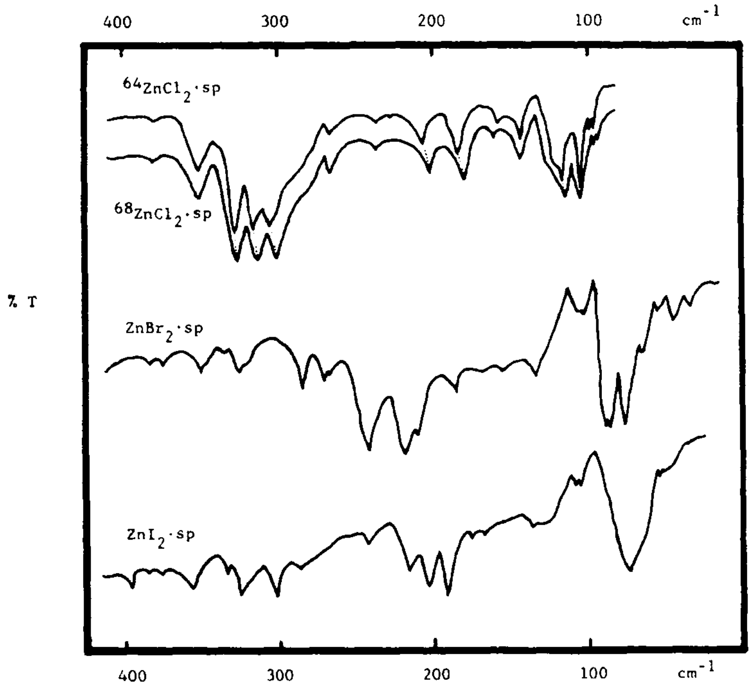

FIGURE 1 The far infrared spectra of zinc halide sparteine complexes.

We can thus assign the Zn–Cl antisymmetric and symmetric stretching frequencies as the strong peaks around 330 and 302 cm^{-1}, respectively (see Figure 1), which shift to 244, 218 cm^{-1} and 216, 191 cm^{-1} for the Zn–Br and Zn–I cases, none of which are present in the spectrum of the free ligand. Furthermore, these absorptions fall into the expected regions for terminal metalhalide stretching bands and predicted frequency ratios of 0.77 – 0.74 for ν(M–Br)/ν(M–Cl), and 0.65 for ν(M–I)/ν(M–Cl).[24] Finally, these values also agree well with those reported by Nakamoto *et al.* for Zn(py)$_2$X$_2$.[23] These assignments, first reported by us in 1974,[1a] have since been confirmed by Choi *et al.*[7e] Cadmium-halide and mercury-halide stretching assignments are made on similar grounds and are also given in Table II.

The X–M–X bending mode is detected with relative ease, since it is not expected to show any appreciable shift by ^{64}Zn-^{68}Zn substitution, but should be sensitive to halogen change. Thus the 120, 115, 104 cm^{-1} absorptions for the zinc chloride complex are lowered to 87, 85, and 76 cm^{-1} for the bromo and to 73 cm^{-1} for the iodo complex. The corresponding bands for the cadmium complexes are 78 cm^{-1}, 67, 64, 58 cm^{-1}, and 59, 57, 51 cm^{-1} for the chloro, bromo, and iodo complexes, respectively, and those for the mercury complexes are 83, 72 cm^{-1}, 74 cm^{-1} and 71, 63 cm^{-1}.

The Zn–N stretching modes are more difficult to assign than the Zn–X modes, since the former are relatively weak. However, the metal isotope technique still shows changes which allow meaningful assignments. Choi[7e] has reported the Zn–N stretching frequencies for ZnCl$_2$ · sp and ZnBr$_2$ · sp as 460, 438 cm^{-1} and 460, 435 cm^{-1}, respectively. Our isotope substitution studies, however, clearly show the Zn–N antisymmetric and symmetric stretching bands for the ^{64}Zn chloro complex to be at 209 and 183 cm^{-1} shifting to 207, 181 cm^{-1} for the ^{68}Zn complex. While the bands assigned by Choi may involve some Zn–N character, we find very definite shifts upon ^{64}Zn-^{68}Zn substitution and conclude that the bands around 209, 183 cm^{-1} must be mainly due to Zn–N bonding. Our assignments correlate well with those of other Zn–N systems such as the Zn(bipy)$_3^{++}$ and Zn(phen)$_3^{++}$ ions,[25] zinc oxinate,[23] Zn(py)$_2$Cl$_2$,[26] and Zn(2,7-dimethyl-1,-8-naphthyridine)$^{++}$.[27] The corresponding bands in the bromo complex appear around 210, 184 cm^{-1}. Those for the zinc iodo complex and all cadmium and mercury complexes are, however, hidden by strong metal-halogen absorptions.

The N–M–N and X–M–N bending modes are weak absorptions and again much less sensitive to metal isotope substitution. Halogen substitution should not affect the former, but the X–M–N mode

might be expected to show some sensitivity.
The assignments given in Table II are tentative, but do show excellent agreement with those of the $Zn(py)_2Cl_2$ system.[26]

The weight of the metal ion shows the expected effect on frequency shifts. As the metal ion is changed from zinc to cadmium to mercury, the metal-halogen bands shift to correspondingly lower frequencies. A similar, but less obvious trend may be detected among the metal-nitrogen modes.

Table III gives the spectral data for sparteine complexes of Co(II), Ni(II), and Cu(II). The Co–Cl antisymmetric and symmetric stretch frequencies appear clearly at 338 and 306 cm^{-1}, respectively, shifting to 256, 235 cm^{-1} and 221, 207 cm^{-1} for the Co–Br and Co–I cases. Again, these are strong

TABLE III

Far infrared frequencies, isotopic shifts, and band assignments for Co^{++}, Ni^{++}, and Cu^{++} sparteine halides, cm^{-1}

	400	M-X	300		200 M-N		100	
Assignment:		ν_a ν_s		ν_a	ν_s δ(N-M-N)	δ(X-M-N) δ(X-	M-X)	
Sp·$CoCl_2$	$\underset{w}{389}$ $\underset{w}{382}$ 353	344 $\underset{s}{\underline{338}}$ 324 317 $\underset{s}{\underline{306}}$	284 268	244 218	185 $\underset{w}{158}$	140 $\underset{s}{\underline{113}}$ $\underset{s}{\underline{102}}$		
Sp·$CoBr_2$	$\underset{w}{382}$ $\underset{w}{376}$ 350	33/ 326 319	286 269 $\underset{s}{\underline{256}}$	$\underset{sh}{\underline{241}}$ $\underset{s}{\underline{235}}$ 220	186 155	130 112	$\underset{s}{\underline{99}}$	
Sp·CoI_2	$\underset{w}{382}$ $\underset{w}{375}$	347 336 324 319	284 269	$\underset{sh}{227}$ $\underset{s}{\underline{221}}$ $\underset{s}{\underline{207}}$	$\underset{w}{185}$ $\underset{w}{176}$ $\underset{w}{166}$	124 112	93 $\underset{s}{\underline{77}}$	
Sp·$^{58}NiCl_2$	$\underset{w}{384}$ 356	346 $\underset{s}{\underline{338}}$ 326 $\underset{s}{\underline{317}}$	$\underset{s}{\underline{296}}$ $\underset{sh}{290}$ 274	248 221	190	$\underset{w}{124}$ $\underset{s}{\underline{108}}$	99 90	
Sp·$^{62}NiCl_2$	384 379 354	346 $\underset{s}{\underline{334}}$ $\underset{s}{\underline{315}}$	$\underset{s}{\underline{297}}$ $\underset{sh}{285}$ 271	$\underset{w}{245}$ 220	186	124 114	99 87 73 $\underset{w}{55}$	34
$\Delta\nu$		4.0 2.0	1.0	1.0	4.0			
Sp·$NiBr_2$	$\underset{w}{382}$ 353	330	294 278 $\underset{s}{\underline{253}}$	$\underset{s}{\underline{240}}$ $\underset{s}{\underline{235}}$ 217	$\underset{w}{186}$ $\underset{w}{162}$	139	$\underset{s}{\underline{87}}$ $\underset{w}{55}$	$\underset{w}{43}$
Sp·NiI_2	$\underset{w}{375}$	331	287 274	246 $\underset{s}{\underline{227}}$ $\underset{s}{\underline{224}}$ $\underset{s}{\underline{201}}$	$\underset{w}{176}$ $\underset{w}{162}$	136 126 109	$\underset{s}{\underline{78}}$	
$CuCl_2$		$\underset{s}{320}$	$\underset{s}{280}$ $\underset{sh}{275}$					
Sp·$CuCl_2$	$\underset{w}{386}$ $\underset{w}{376}$ 352	$\underset{w}{324}$	$\underset{s}{\underline{298}}$ 288 $\underset{s}{\underline{274}}$ $\underset{sh}{264}$	232 211	191			
Sp·$CuBr_2$	$\underset{w}{385}$ $\underset{w}{374}$ $\underset{w}{356}$	$\underset{w}{339}$ $\underset{w}{330}$	292 270	$\underset{s}{\underline{248}}$ 235 $\underline{219}$	193 181 $\underset{s}{158}$	123 105	85 $\underset{w}{55}$	
α-isoSp·$CuCl_2$	384 365	338	$\underset{s}{\underline{298}}$ $\underset{s}{285}$ $\underset{s}{\underline{275}}$	251 227 210				
β-isoSp·$CuCl_2$	407 373	306	$\underset{s}{\underline{282}}$ $\underset{s}{\underline{275}}$	213	204 186 154	133	99 97 87 83 79	$\underset{w}{43}$
β-isoSp·$CuBr_2$	374	$\underset{w}{338}$ $\underset{w}{320}$ $\underset{s}{302}$	276 270 258	250 $\underset{s}{\underline{229}}$ $\underset{s}{\underline{218}}$ $\underset{sh}{209}$				
Sp·$CuCl_4^=$	$\underset{w}{386}$ 350	$\underset{s}{\underline{306}}$	$\underset{sh}{292}$ $\underset{w}{277}$ $\underset{s}{\underline{257}}$	$\underset{w}{228}$	188 158	$\underset{s}{142}$ 108	74	
Sp·$CuBr_4^=$	$\underset{w}{386}$	349 319	293 277	$\underset{s}{\underline{247}}$ $\underset{w}{228}$	$\underset{s}{\underline{198}}$ 176 153	125 109	100 79	
Sp·$AuCl_3$	396 $\underset{sh}{363}$ $\underset{s}{\underline{353}}$	309	$\underset{w}{275}$	245	$\underset{w}{204}$ $\underset{w}{167}$	144 139 125 108	83 70	

ν_a = antisymmetric stretch
ν_s = symmetric stretch
δ = bending mode
w = weak band
s = strong band
$\Delta\nu = \nu_{^{58}Ni} - \nu_{^{62}Ni}$
M–X bands are underlined

absorptions not observed in the spectrum of the parent ligand, and the ν(Co–Br)/ν(Co–Cl) and ν(Co–I)/ν(Co–Cl) ratios fall within expected values. The absence of stable cobalt isotopes prevents metal isotope studies, however, the assigned Co–Cl values correspond closely to the 347, 306 cm^{-1} values reported for $Co(py)_2Cl_2$.[28]

The nickel-halide absorption bands may be assigned on the basis of absorption intensity, and shifts caused by halogen and metal isotope substitution. The assignments compare very favorably with those reported for the nickel-halide absorptions in $Ni(PPh_3)X_2$.[23,29] In this one case of nickel most bands appear to be shifted by isotopic substitution. This is likely due to a crystal modification (see Synthesis of Complexes). It is also noteworthy that three M–X stretching bands are observed in many compounds. This may suggest a polymeric or other structure rather than a simple chelate,[30] however, the only available crystal structure for a sparteine metal complex[7c] does not indicate this.

The Cu–Cl absorptions (assigned previously[1c]) are lowered by the predicted ratio to the Cu–Br values of 248 and 219 cm^{-1} (229 and 204 for the β-isosparteine complex). The decreasing stability of the α-isosparteine, sparteine and β-isosparteine copper(II) chloride complexes has been discussed[1c] on the basis of stereochemical and hydrolysis results. The Cu–Cl frequencies shown here for the three diastereoisomer complexes appear to be decreasing in the same direction, thus confirming the trend in stability. The copper-halide assignments for the copper tetrahalo complexes are also based on the intensity of absorption and the expected shifts between chloro and bromo complexes. However, the gold-chloride absorption appears to be out of line. The heavy gold ion would be expected to produce a low gold-chloride absorption frequency, however, the higher charge on gold(III) appears to have the opposite effect. The intensity of the 353 cm^{-1} absorption suggests it as the Au–Cl stretching frequency.

Again the metal-nitrogen absorptions are much less pronounced and the assignments correspondingly more difficult. Nevertheless, the assignments given in Table III are based on metal isotope shifts for the nickel chloro complex and comparisons with published assignments from other complexes.[23,25,27]

It is of interest to compare the metal-ligand bonding properties for the Co(II), Ni(II), Cu(II), and Zn(II) complexes. There is an increase in metal-nitrogen frequency (indicating stronger bonding) from cobalt to nickel, a very sharp increase with copper (to 468, 436 cm^{-1}),[1c] followed by a return to lower values with the zinc complex (see Table II). At the same time, the metal-halide frequency drops from cobalt to nickel and plunges to a low value at copper and with zinc returns to a higher value. It is interesting that the ionic radii for these metal ions change in the same manner: Co > Ni > Cu < Zn. Apparently the size of copper(II) allows for the best fit in the sparteine cage. A good fit ensures a strong Cu–N bond, which in turn drains electrons sufficiently away from the Cu–Cl environment to cause a corresponding weakening of the Cu–Cl bond. This contention was tested, and confirmed, by comparing the Cu–Cl and Hg–Br absorption bands (see Tables III and II, respectively) for the simple salts with those of the complexed salts. Upon complexation the Cu–Cl absorptions move from 320, 280 cm^{-1} to 298, 288, 274 cm^{-1}, and that for Hg–Br from 249 to 196 cm^{-1}. Electronic effects of this nature have been observed in metal carboxylic ester[31] and metal sulfoxide complexes.[32,33] Further substantiating evidence for a strong Cu–N bond and weak Cu–Cl bond comes from crystallographic studies on the copper chloro complex of the beta isomer, which shows 1.994 Å for the Cu–N distance and 2.255 Å for Cu–Cl.[7c]

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1. a) Presented, in part, before the XV International Conference on Coordination Chemistry, Moscow, USSR, June, 1973; see Proceedings Vol. 1, p. 285, No. III-43; and, in part, before the 8th Great Lakes Regional Meeting of the ACS, Lafayette, Ind., June, 1974; see Abstracts INORG No. 134.

   b) Supported by grants from Eli Lilly and Company, Indianapolis, Ind., and the Indiana University Foundation.

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