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Alkaloids as Ligands. 1. Synthesis and Characterization of Three Cobalt(II) Pseudohalide Compounds Containing *l*-Sparteine

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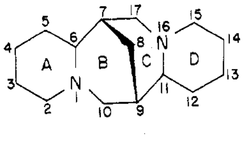
Received July 14, 1976 AIC60509C

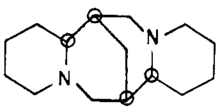
The alkaloid *l*-sparteine (sp) combines with cobalt(II) cyanate, thiocyanate, and selenocyanate to form pseudotetrahedral, N-bonded four-coordinate complexes of the type $Co(sp)(NCX)_2$ (X = O, S, or Se). Their electronic spectra indicate that $Co(sp)(NCSe)_2$ is nearly tetrahedral whereas $Co(sp)(NCO)_2$ and $Co(sp)(NCS)_2\cdot{}^1/_2H_2O$ are more severely distorted from tetrahedral geometry. This distortion is observed in the low-symmetry splitting of the ν_2 and ν_3 ligand field transitions which is ca. twice as large in the isocyanate and isothiocyanate complexes as in the isoselenocyanate complex which exhibits a splitting of ca. 2000 cm^{-1} for ν_2 and 1000 cm^{-1} for ν_3. Apparently the isoselenocyanate complex maintains a nearly regular tetrahedral geometry by changing the conformation of the A ring of *l*-sparteine from the chair to the boat conformation. Pseudohalide stretching and bending modes are identified and found to be similar to those of other complexes containing nitrogen-coordinated pseudohalides. For the isocyanate, isothiocyanate, and isoselenocyanate compounds cobalt–tertiary nitrogen stretching frequencies are 465, 498, and 473 cm^{-1}, respectively. Below 400 cm^{-1} two cobalt–pseudohalide nitrogen stretching bands for each compound are identified.

Introduction

Although many alkaloids have donor groups which can bind to metal ions, only a few of these potentially interesting ligands have come to the attention of coordination chemists. One exception which has recently generated interest is sparteine (I), a member of the lupine alkaloid family.[1] Several studies[2–6] have established that all three of the configurational isomers of I are capable of forming stable complexes with both group 2A and first-row transition metal ions. These three conformational isomers are named β-isosparteine [(6*S*,7*S*,9*S*,11*S*)-sparteine (II)], sparteine [(6*R*,7*S*,9*S*,11*S*)-sparteine (III)], and α-isosparteine [(6*R*,7*S*,9*S*,11*R*)-sparteine (IV)]. The levo enantiomer of III, the subject of this report, is a viscous oil at room temperature with the principal conformation V.[1]



I



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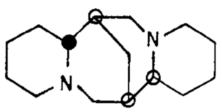

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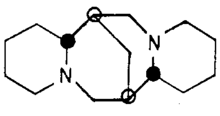

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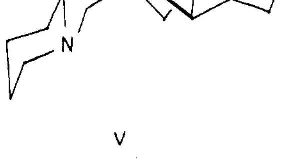
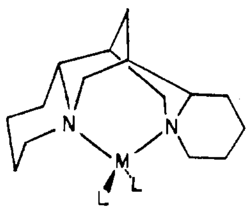
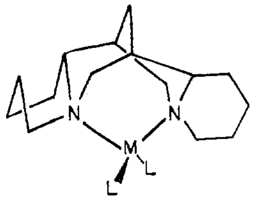


V

Although V is the preferred conformation of neat *l*-sparteine, it acts as a bidentate ligand toward metal ions[2–6] forming complexes with the stereochemistry of VI. Structure VI may represent only one of several conformations of *l*-sparteine in its metal complexes. A second example is VII where ring A takes on a boat conformation. The actual conformation of *l*-sparteine in its metal complexes should be quite sensitive to both the metal and L. In this paper we present spectroscopic and magnetic measurements on three cobalt(II) pseudohalide complexes of *l*-sparteine (sp) which indicate the overall stereochemistry of VI.



VI



VII

Experimental Section

Materials. *l*(–)-Sparteine free base was obtained from Sigma Chemical Co. and used without further purification. Cobalt(II) chloride hexahydrate was recrystallized once prior to use. The hydrated cobalt(II) pseudohalides used in the subsequent preparations were prepared as needed by grinding stoichiometric amounts of $CoCl_2\cdot 6H_2O$ and potassium or sodium pseudohalide together in a mortar, taking up the mixture in methanol, filtering, and removing the solvent. All other chemicals and solvents were the best commercially available.

$Co(sp)(NCS)_2\cdot{}^1/_2H_2O$. The diisothiocyanato((6*R*,7*S*,9*S*,11*S*)-*l*-sparteine)cobalt(II) hemihydrate complex was prepared by dissolving 1 mmol of cobalt(II) thiocyanate in the minimum amount of boiling methanol. This solution was dehydrated by refluxing with 5 mL of 2,2-dimethoxypropane. A solution of *l*-sparteine in anhydrous methanol was added drop by drop to the solution of cobalt(II) thiocyanate. Initially a small amount of green material separated from the resulting deep blue solution. This green material, which may be $Co(sp)(NCS)_2\cdot nH_2O$, was collected by suction filtration and the filtrate set aside for several days. After this time, the blue crystals which had separated were collected and washed with methanol. After drying at room temperature the preparation analyzed as the hemihydrate. Anal. Calcd for $CoC_{17}H_{27}N_4S_2O_{0.5}$: Co, 14.08; C, 48.79; H, 6.50; N, 13.39. Found: Co, 14.1; C, 48.94; H, 6.40; N, 13.38.

$Co(sp)(NCO)_2$. The diisocyanato((6*R*,7*S*,9*S*,11*S*)-*l*-sparteine)cobalt(II) complex was prepared in an exactly analogous manner to $Co(sp)(NCS)_2\cdot{}^1/_2H_2O$. The anhydrous product is deep blue but has a slight purple hue in artificial light. Anal. Calcd for $CoC_{17}H_{26}N_4O_2$: Co, 15.62; C, 54.11; H, 6.95; N, 14.85. Found: Co, 15.6; C, 54.38; H, 7.12; N, 14.80.

$Co(sp)(NCSe)_2$. The diisoselenocyanato((6*R*,7*S*,9*S*,11*S*)-*l*-sparteine)cobalt(II) complex, prepared in a manner analogous to $Co(sp)(NCS)_2\cdot{}^1/_2H_2O$, was isolated by evaporation at room temperature. The reaction product was extracted with benzene to remove any uncomplexed sparteine which is soluble in benzene. A bluish green anhydrous oil was obtained. Anal. Calcd for $CoC_{17}H_{26}N_4Se_2$: Co, 11.71; C, 40.57; H, 5.21; N, 11.13. Found: Co, 12.6; C, 41.02; H, 5.20; N, 11.09.

Analytical Methods. Cobalt was determined by atomic absorption with a standard deviation of ±0.2% except in the case of the isoselenocyanate complex which gave results reproducible to ±1.5%. This behavior may be due to the possible interference of selenium. Although selenium does not have an absorption line which would interfere with the cobalt absorption line, it is possible that the acid oxidation product SeO_2 might be aspirated into the flame in an irreproducible manner causing an error in these analyses.

Physical Measurements. Infrared spectral data were obtained at 40 °C on a Perkin-Elmer 180 with polystyrene as an external calibrant and are reproducible to 1 cm^{-1} or better throughout the entire spectral range. Integrated absorption measurements in the C═N stretching region were performed in dichloromethane over the solution concentration range of $(1-5) \times 10^{-4}$ M. The integrated intensities were calculated by using the Lorenz function (1) where K' is the Ramsay

$$A'_{CN} = \frac{K'}{cl} \ln\left(\frac{I_0}{I_{max}}\right)\Gamma_{1/2} \tag{1}$$

constant,[7] $\ln(I_0/I_{max})$ is the peak intensity, c is the molar concentration, l is the cell path length in centimeters, and $\Gamma_{1/2}$ is the half-width of the band at half-maximum. The values of A'_{CN} were obtained by using separately weighed samples and are accurate to ±5%.

Electronic spectra were recorded on a Cary 14 spectrophotometer. The molar extinction coefficients are the apparent absorptivities per mole of complex measured at the apparent band maximum. Oscillator strengths were calculated[8] with eq 2 where the integration is over the

$$f = 4.32 \times 10^{-9} \int_{\sigma_2}^{\sigma_1} \epsilon(\sigma)\, d\sigma \tag{2}$$

entire 5000–40 000 cm^{-1} region and $\epsilon(\sigma)$ is the molar absorptivity at a given frequency, σ. In order to determine $\epsilon(\sigma)$ the experimental spectra were fit numerically to a four-parameter equation[9] by using the program BIGAUSS.[10] Subsequent work revealed that the spectra could better be expressed by a three-parameter symmetric Gaussian function[11] (3) where $\epsilon(\sigma_{max})$ is the maximum molar absorptivity of

$$\epsilon(\sigma) = \epsilon(\sigma_{max})[2^{-(\sigma-\sigma_{max})\Gamma_{1/2}{}^2}] \tag{3}$$

the band and $\Gamma_{1/2}$ is the half-width of the band at half-maximum intensity. The values used to calculate f are derived from a least-squares fit to (3).

Electronic spectra were measured at ambient and liquid hydrogen temperature (23 K) by using an Air Products AC-2 Cyro-Tip refrigerator. Spectra recorded in Kel F-90 grease mulls were measured against a Kel F-90 reference blank. The spectra obtained in KBr pressed pellets were obtained as described elsewhere.[12] These spectra were essentially identical with their respective solution and mull spectra.

Magnetic susceptibility measurements at five different fields were obtained on a standard Gouy balance calibrated with $HgCo(NCS)_4$. Diamagnetic corrections for the ligands were calculated from tables of Pascal's constants.[13]

Results and Discussion

The new compounds are soluble in a wide range of solvents. The dark blue $Co(sp)(NCO)_2$ and $Co(sp)(NCS)_2 \cdot {}^1/_2H_2O$ and the dark blue-green $Co(sp)(NCSe)_2$ are very soluble and stable over many months in dry halocarbon solvents such as dichloromethane and chloroform. However, these compounds decompose rapidly when dissolved in polar solvents such as water, dimethylformamide, or dimethyl sulfoxide and decompose slowly in nonanhydrous solvents.

On several occasions, in an attempt to recrystallize the $Co(sp)(NCS)_2 \cdot {}^1/_2H_2O$ compound, we were able to isolate a viscous blue oil which could be dehydrated over P_2O_5 to give the original compound. This blue oil may be a higher hydrate of the original hemihydrate. If the methanol used is not entirely free of water, a green precipitate is obtained which gives irreproducible analyses. The infrared spectrum of this precipitate indicates the presence of both coordinated water and pseudohalide. These materials most likely have the formulation $Co(sp)(NCS)_2 \cdot nH_2O$. We do not pursue these compounds further except to mention their infrared spectra.

Infrared Spectra. The infrared spectra of sparteine and its metal complexes are characterized by a large number of moderately intense, sharp bands. The appearance of these bands is expected because of the large number of vibrational modes allowed for these compounds. We need not consider most of these bands because they are unaffected by the coordination of sparteine to metal ions. However, changes in the position and intensity of some of these bands upon complexation provide insight into the bonding in these compounds.

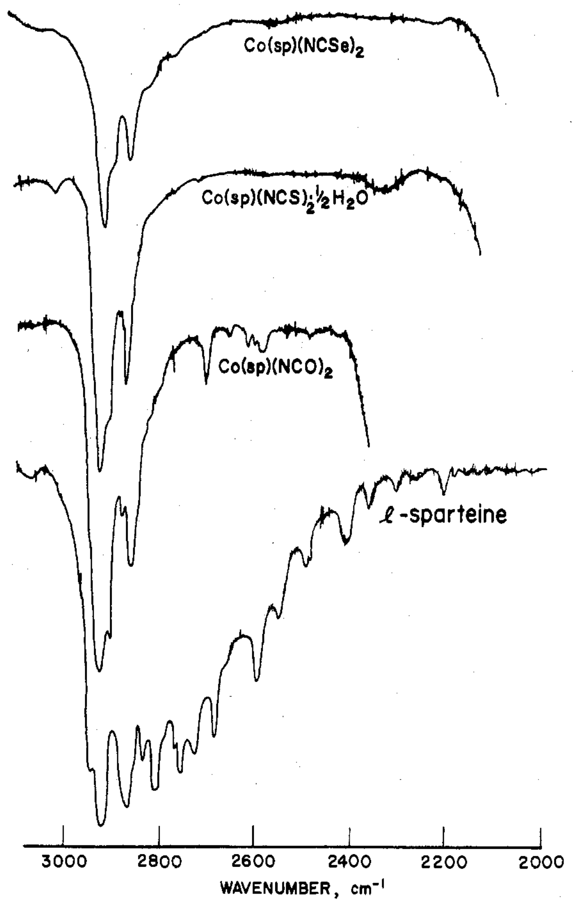
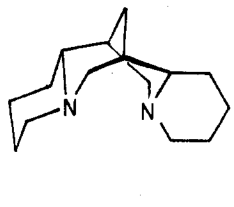


Figure 1. Infrared spectral bands in the carbon–hydrogen stretching region, recorded in CsI at 40 °C.

Figure 1 shows the region of the infrared spectra of l-sparteine and its cobalt(II) pseudohalide complexes within which the carbon–hydrogen vibrational bands occur. The complexes of l-sparteine display these bands in the 3000–2800-cm^{-1} region whereas l-sparteine has a number of these bands extending down to 2500 cm^{-1}. These low-frequency C–H stretching bands are called "trans bands".[14] Originally, the appearance of these trans bands was thought to require the presence of at least two hydrogens which were both α and trans-diaxial to the lone pair of electrons on the tertiary nitrogen atoms.[14] Wiewiorowski et al.[15,16] later restated the earlier criterion to require the presence of only one trans-diaxial α hydrogen for the observation of the trans bands. According to Wiewiorowski et al.,[16] "The general complexity and intensity of this absorption [the trans bands] will be roughly proportional to the number of *trans*-diaxial (antiparallel) α-hydrogens." The presence of trans bands in the spectrum of neat l-sparteine (Figure 1) supports conformation V—where ring C adopts a boat conformation—over conformation VIII—where ring C



VIII

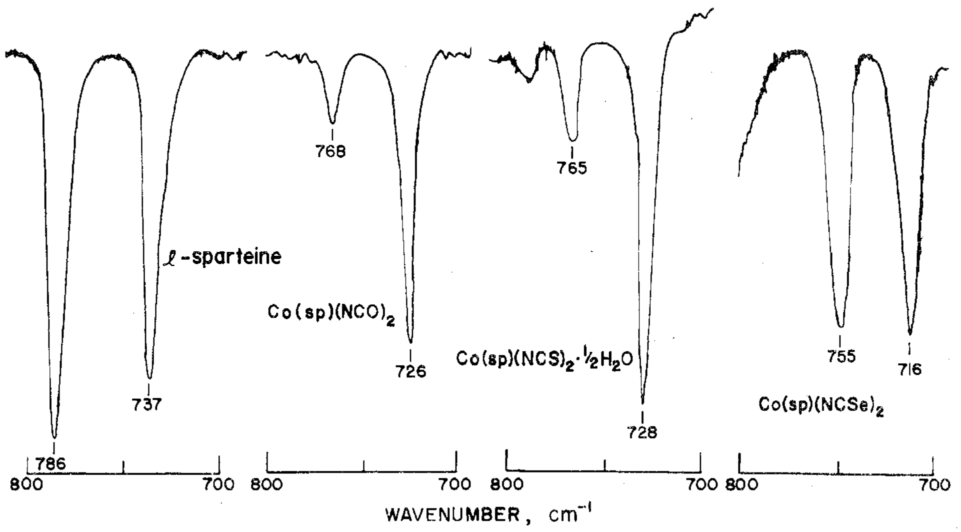


Figure 2. Infrared spectral bands in the carbon–hydrogen deformation region, recorded in CsI at 40 °C.

Table I. Carbon–Hydrogen Deformation Bands Observed at 40 °C (in cm^{-1})

Compd	Matrix	δ_1	δ_2	$\Delta\delta_1$	$\Delta\delta_2$	$\Delta\delta_1/\Delta\delta_2$[a]	$F_{\delta_1}/F_{\delta_2}$[b]
Sparteine	Neat	786	737	0	0		1.15
Co(sp)(NCO)$_2$	CsI	768	726	−18	−11	1.64	0.30
Co(sp)(NCS)$_2$·$^1/_2$H$_2$O	CsI	765	728	−21	−9	2.33	0.26
Co(sp)(NCSe)$_2$	Neat	755	716	−31	−21	1.48	0.60
Co(sp)(NCS)$_2$·*n*H$_2$O	CsI	752	712	−34	−25	1.36	0.56

[a] ±0.2. [b] Areas obtained by weighing.

takes on a chair formation. Rather more esoterically, conformation V would be favored over conformation VIII because of the severe lone pair–lone pair repulsion to be found in VIII.

The infrared spectra of the cobalt(II) pseudohalide complexes show no signs of the trans bands. The absence of the trans bands is expected because the nitrogen lone-pair electrons are involved in metal coordination. Unfortunately, the lack of trans bands does not in itself establish the conformation of the *l*-sparteine ligand in these complexes. It does however establish that both of the nitrogen atoms are coordinated because the Wiewiorowski criterion[16] would allow for the appearance of trans bands even if only one nitrogen were coordinated.

Further information about the conformation of *l*-sparteine in these complexes may be obtained from the other infrared bands which are influenced by coordination. Two such bands are shown in Figure 2 and numerical data are presented in Table I. The frequency and intensity of these bands are characteristic of carbon–hydrogen deformation absorption bands although their specific assignments are uncertain. Table I lists the higher energy band as δ_1, the lower energy band as δ_2, and F_{δ_1} and F_{δ_2} as the relative areas of these two bands. Upon complexation, these two bands shift by $\Delta\delta_1$ and $\Delta\delta_2$ to lower energy. The magnitude and direction of these shifts indicate a weakening of the hydrogen–nitrogen lone-pair interactions. A similar shift is observed in the infrared spectra of several Fe(II) complexes containing *l*-sparteine.[17]

An examination of a HGS model of *l*-sparteine in conformation V reveals considerable steric interaction between the lone pair of electrons on nitrogen 1 (N1) and both the 17β hydrogen (17βH) and 11 hydrogen (11H). Models also reveal that this interaction is reduced upon coordination if the stereochemistry of the complex is either VI or VII. Because we cannot determine the band purity of δ_1 and δ_2, it is difficult to assign them to either the 17βH–C or the 11H–C bend. However, we suggest that δ_1 describes the 11H–C bend and δ_2 the 17βH–C bend because the models show that 11H is closer to N1 than is 17βH.

The infrared spectra of the cobalt(II) pseudohalide complexes contain the bands listed in Table II which may be assigned to the pseudohalide ligands.[18] Although in some cases it is possible to determine the exact mode of pseudohalide coordination from frequency data, it is desirable to obtain intensity data for the absorption of interest. This technique has been used to verify the existence of linkage isomers in various platinum(II) thiocyanate–isothiocyanate complexes[19,20] and in two Cu(II) complexes.[21] The review by Burmeister[22] has shown that the integrated absorption intensity of ν_{CN} for N-bonded pseudohalides is usually in the range of (1–4) × 10^5 cm^{-2} M^{-1} whereas the X-bonded pseudohalides have intensities

Table II. Metal–Ligand and Pseudohalide Infrared Bands (in cm^{-1})

Compd	Temp, K	Matrix	$\nu_{a(N-CX)}$	$\nu_{s(NC-X)}$	δ_{NCX}	$\nu_{Co-N(sp)}$	ν_{Co-NCX}
Co(sp)(NCO)$_2$	313	CH$_2$Cl$_2$ soln	2280	1346	*a*		
	313	CsI	2280	1350	617	465	385, 350
	78	CsI	2280	1348	618		
Co(sp)(NCS)$_2$·$^1/_2$H$_2$O	313	CH$_2$Cl$_2$ soln	2051	*a*	*a*		
	313	CsI	2050	853	490	498	320, 310
	313	KBr	2052	853	490		
	78	KBr	2055	853	490		
Co(sp)(NCSe)$_2$	313	CH$_2$Cl$_2$ soln	2072	620	*a*		
	313	CsI	2060	620	*a*	473	270, 240
	78	CsI	2058	620	*a*		
Co(sp)(NCS)$_2$·*n*H$_2$O	313	CsI	2060	843	490		

[a] Not observed.

Table III. Magnetic Susceptibility Data

Compd	T, K	$10^6\chi_M'$, cgsu	μ_{eff}, μ_B
$Co(sp)(NCO)_2$, $\chi^c_M = -286$ cgsu	298.3	8 828	4.59
	243.6	10 486	4.52
	165.5	14 820	4.43
	140.0	17 820	4.47
	102.2	22 950	4.33
$Co(sp)(NCS)_2 \cdot {}^1/_2H_2O$, $\chi^c_M = -289$ cgsu	296.2	8 910	4.59
	239.0	10 550	4.49
	170.0	14 405	4.43
	135.0	18 355	4.45
	99.3	23 703	4.37

of approximately 0.1×10^5 cm^{-2} M^{-1}. The three cobalt(II) pseudohalide complexes of *l*-sparteine all have an intensity value of ν_{CN}, A'_{CN}, indicative of N bonding. The specific values obtained in dichloromethane are as follows: $Co(sp)(NCO)_2$, 2.3×10^5 cm^{-2} M^{-1}; $Co(sp)(NCS)_2 \cdot {}^1/_2H_2O$, 1.4×10^5 cm^{-2} M^{-1}; $Co(sp)(NCSe)_2$, 0.85×10^5 cm^{-2} M^{-1}.

Choi et al.[4] have assigned both metal–nitrogen and metal–halogen stretching frequencies for the copper(II) and zinc(II) chloride and bromide complexes of *l*-sparteine. They assigned weak bands at 435–440 and 460–470 cm^{-1} to the metal–sparteine nitrogen stretching absorption bands. Boschmann et al.[3] have confirmed these band assignments by using the pure metal isotope shift technique.[23] We make similar assignments which are also presented in Table II. These data are in essential agreement with results presented earlier[24] for compounds containing both Co–NCX and Co–N (tertiary nitrogen) bonds.

Magnetic Susceptibility Studies. Because $Co(sp)(NCSe)_2$ is an oil at room temperature we found it difficult to obtain magnetic susceptibility data for this compound. Therefore, only the results for the isocyanate and the isothiocyanate compounds are reported in Table III. The values of μ_{eff} at room temperature are very close to the spin-only value expected for a tetrahedral d^7 metal complex. This establishes the ground state in these materials as a spin quartet. The slight temperature dependence of μ_{eff} is consistent with the type of behavior expected for a distorted tetrahedral ligand field about the cobalt atom.[25]

Electronic Spectral Data. Figure 3 shows the electronic spectra of the cobalt(II) pseudohalide complexes. Table IV presents numerical data for the three complexes.[26] The appearance of two sets of bands, one centered near 8000 cm^{-1} and the other near 16 000 cm^{-1}, in conjunction with the values of the apparent molar extinction coefficients, is indicative of pseudotetrahedral cobalt(II).[27] However, the large splittings observed in Figure 3 for these bands are indicative of a much lower than tetrahedral ligand field symmetry, presumably a result of the dissimilar ligands.[28] Mason and Peacock[2] have observed similar splittings for the cobalt(II) halide complexes of *l*-sparteine. Similar large splittings have also been observed[29,30] in several cobalt halide complexes with bulky tertiary amine ligands.

We have calculated the tetrahedral crystal field parameters, Dq and β_{35}, by using the equations of König[31] and by taking the center of the three bands located at ca. 10 000 cm^{-1} as ν_3. The results are presented in Table V. This table also includes the parameters for the cobalt halide complexes calculated with the same model and the experimental spectra obtained by Mason and Peacock.[2] Although one may question the validity of this tetrahedral model calculation because the derived values depend markedly upon the values used for ν_2 and ν_3, this model serves as a useful starting point for calculations which include lower symmetry distortion parameters. Lever and Nelson[32] have discussed the trends in Dq and B_{35} for a lengthy series of $Co(amine)_2X_2$ compounds. They observed an increase in Dq as a function of the crystal field strength of X in agreement with the trends in the classical spectrochemical series;[33] namely, Dq increases in the order $I^- < Br^- < Cl^- < {}^*NCS^- < {}^*NCO^- < {}^*NCSe^-$. Our data, along with those of Mason and Peacock,[2] further illustrate this trend (Table V). The one notable exception is $Co(sp)(NCSe)_2$. This exception may be due to the steric influence of the bulky amine ligands as discussed by Lever and Nelson.[32] The unusually small value of Dq for $Co(sp)(NCSe)_2$ is consistent with the presence of a smaller low-symmetry ligand field as is indicated by the smaller splittings of the ν_2 and ν_3 bands in this compound (see Figure 3). This smaller distortion may result from reduced steric hindrance in $Co(sp)(NCSe)_2$ as compared to the NCO and NCS complexes. We believe that the NCSe ligand forces conformation VII to be preferred over conformation VI thus relieving the rather severe repulsion between the hydrogen atoms of ring A and the isoselenocyanate ligand. This different conformation may explain why the isoselenocyanate compound is an oil at room temperature.

In the absence of polarized spectral data it is difficult to assign the components of ν_2 and ν_3 with certainty. Ideally, C_{2v} symmetry splits the terms associated with ν_2 and ν_3 into their full complements of terms as shown in Figure 4a. The derived symmetry labels are referred to the coordinate system illustrated in Figure 4b. If this is the correct ordering scheme for the electronic states of the $Co(sp)(NCX)_2$ compounds, the following assignments can be made for the transitions from

Table V. Ligand Field Parameters Derived from the Tetrahedral Model

Compd	Matrix	Temp, K	$\nu_2$obsd, cm^{-1}	$\nu_3$obsd, cm^{-1}	Dq, cm^{-1}	β_{35}[a]
$Co(sp)Cl_2$[b]	$CHCl_3$ soln	Amb			510	0.62
$Co(sp)Br_2$[b]	$CHCl_3$ soln	Amb			490	0.62
$Co(sp)I_2$[b]	$CHCl_3$ soln	Amb			470	0.61
$Co(sp)(NCO)_2$	$CHCl_3$ soln	Amb	9025	17 725	530	0.64
	CH_2Cl_2 soln	Amb	9025	17 675	530	0.64
	CH_3NO_2 soln	Amb	9050	17 725	530	0.64
	Kel-F mull	Amb	9250	17 650	550	0.64
	KBr	Amb	9100	19 100	530	0.74
	KBr	23	9050	19 100	530	0.74
$Co(sp)(NCS)_2 \cdot {}^1/_2H_2O$	$CHCl_3$ soln	Amb	9375	15 025	590	0.40
	KBr	Amb	9400	17 360	560	0.60
	KBr	23	9400	17 350	560	0.60
$Co(sp)(NCSe)_2$	CH_2Cl_2 soln	Amb	8000	16 025	470	0.60
	Neat	Amb	7800	16 325	460	0.62
	Neat	23	7775	16 350	460	0.62

[a] Value of $B_{\text{free ion}} = 1115$ cm^{-1}, taken from ref 11, p 437. [b] Experimental data taken from ref 2.

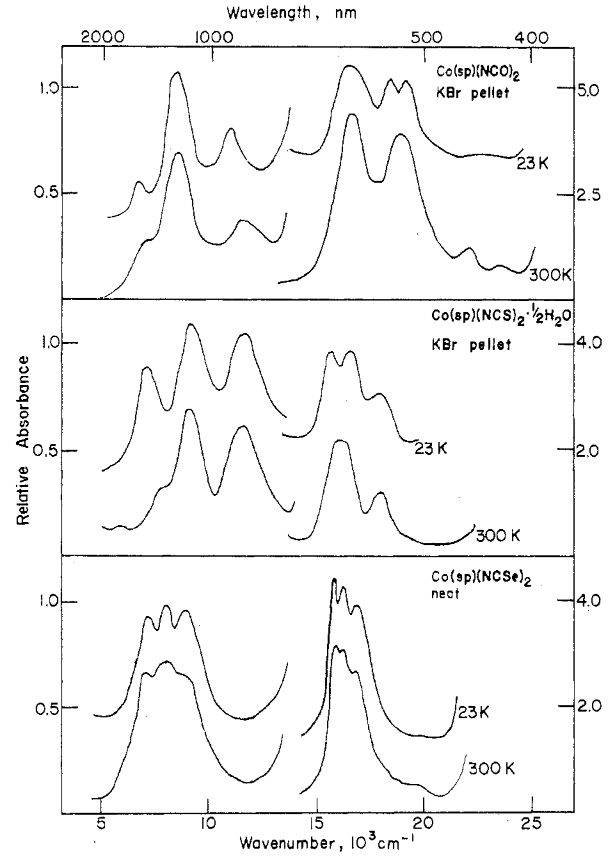


Figure 3. Electronic absorption spectra in the near-infrared and visible region.

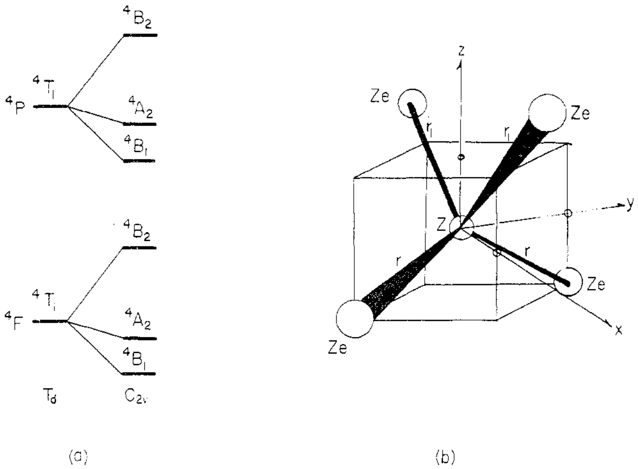


Figure 4. (a) Term energy diagram showing the behavior of tetrahedral $^4T_1(F)$ and $^4T_1(P)$ terms in a C_{2v} ligand field. (b) Coordinate system corresponding to model 2.

the $^4A_2$ ground term to the components of the $^4T_1(F)$ term. The low-intensity band at ca. 7000 cm^{-1} corresponds to the transition $^4A_2 \rightarrow {}^4B_1$; the most intense band at ca. 8000–9000 cm^{-1} is $^4A_2 \rightarrow {}^4A_2$; and the highest energy band of the set corresponds to the $^4A_2 \rightarrow {}^4B_2$ transition. Similar assignments can also be made for the three component bands of $^4A_2 \rightarrow {}^4T_1(P)$, ν_3, between 16 000 and 22 000 cm^{-1}.

In an attempt to account for the different band splittings observed in the spectra of these compounds, we have calculated the various ligand field parameters employing the conventional model of Flamini et al.[34] and the variable-charge, tetrahedral-geometry (VCTG) model of Menzel et al.[35] The results are given in Table VI.[26] In both models the distortion parameters, *Ds* and *Dt*, are much larger for the isocyanate and the isothiocyanate complexes than for the isoselenocyanate complex. The parameter *Ds* calculated by using model 1[34] is −1860 cm^{-1} for Co(sp)(NCO)$_2$, −760 cm^{-1} for Co(sp)(NCS)$_2$·$^1/_2$H$_2$O, and −320 cm^{-1} for Co(sp)(NCSe). A similar situation is found for *Dt*, which, for model 1, is greater than 4000 cm^{-1} for the first two compounds but ca. 3450 cm^{-1} for the last compound. Because the absolute values of these parameters are subject to considerable error, we can only ascribe significance to their relative values. However, it is important to note that both models indicate that Co(sp)(NCO)$_2$ and Co(sp)(NCS)$_2$·$^1/_2$H$_2$O are more distorted than Co(sp)(NCSe)$_2$. Both models account equally well for the splitting observed in the spectrum of Co(sp)(NCSe)$_2$. The calculated energy levels in this case agree with the observed levels to within experimental uncertainty. On the other hand, these models do not adequately account for the splitting observed in the spectra of Co(sp)(NCO)$_2$ and Co(sp)(NCS)$_2$·$^1/_2$H$_2$O. The slightly better fit of the Menzel et al. model[35] over that of the Flamini et al. model[34] is not surprising because the former implicitly accounts for covalency effects while the latter does not. The inability of these models to account for the splitting in the spectra of Co(sp)(NCO)$_2$ and Co(sp)(NCS)$_2$·$^1/_2$H$_2$O is most likely due to the extensive distortion of these compounds from C_{2v} symmetry.

Conclusions

We have shown that the tetracyclic tertiary diamine alkaloid *l*-sparteine forms four-coordinate pseudotetrahedral complexes with Co(NCO)$_2$, Co(NCS)$_2$, and Co(NCSe)$_2$. These compounds are formulated as Co(sp)(NCX)$_2$. The absence of certain carbon–hydrogen stretching bands, known as trans bands, and an analysis of the carbon–hydrogen deformation bands indicate that the sparteine molecule acts as a bidentate ligand. Infrared absorption intensity measurements indicate that the pseudohalide is N bonded to cobalt.

We found that the current models[34,35] for C_{2v} complexes could not satisfactorily account for the splitting observed in the ligand field spectra of Co(sp)(NCO)$_2$ and Co(sp)(NCS)$_2$·$^1/_2$H$_2$O. That the ligand field spectrum of Co(sp)(NCSe)$_2$ may be interpreted in terms of these models indicates that the isoselenocyanate ligand may be able to force the sparteine ligand to adopt conformation VII in preference to conformation VI.

Acknowledgment. The financial assistance which was provided by the National Science Foundation through Grants GP-8653, GY-6625, and CHE-75-20417 is gratefully appreciated.

Registry No. Co(sp)(NCS)$_2$, 61477-61-0; Co(sp)(NCO)$_2$, 61477-62-1; Co(sp)(NCSe)$_2$, 61477-63-2; Co(sp)Cl$_2$, 39733-81-8; Co(sp)Br$_2$, 39733-82-9; Co(sp)I$_2$, 39733-83-0; *l*-sparteine, 90-39-1.

Supplementary Material Available: Listings of electronic spectral data, Table IV, and calculated crystal field parameters, Table VI (3 pages). Ordering information is given on any current masthead page.

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Notes

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Solution Dynamics of Tris(acetylacetonato)chromium(III)

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Received May 28, 1976 AIC60401X

Studies of the solution dynamics of transition metal complexes are important in understanding the catalytic activity of metal ions in both biological and nonbiological systems.[1] In particular, we are interested in the chemical dynamics of first and second coordination sphere exchange of ligands with bulk solvent molecules. Such studies are capable of exploring the rate, order, and preferential orientation of exchanging species in the first and second coordination sphere and relating these parameters to intrinsic properties such as ion size and charge, steric factors of association between the metal ion complex and solvent molecules, and dipole moment and hydrogen-bonding ability of the solvent.[2-4]

Certain paramagnetic complexes such as tris(acetylacetonato)chromium(III), $Cr(acac)_3$, have been used extensively as spin relaxants in carbon-13 Fourier-transform NMR studies. The controversy and questions which have arisen over their use are intimately associated with the first and second coordination sphere behavior of the solvent and solute molecules about the paramagnetic complex.[5-11] It has been postulated that while the spin–lattice and spin–spin relaxation times of the carbon-13 species are reduced in the presence of Cr(III) complexes and the NOE (nuclear Overhauser effect) is quenched, the chemical shift is unaffected. Our previous studies of the solution dynamics of tris(ethylenediamine)chromium(III) and hexakis(dimethyl sulfoxide)chromium(III) indicate that this assumption may not be true.[12,13]

Here we report the dependence of the chemical dynamics of first and second coordination sphere exchange of $Cr(acac)_3$ with four solvents on various properties of the solvents such as dipole moment, basicity, and hydrogen-bonding ability. In addition to its role as a spin relaxant, $Cr(acac)_3$ was chosen for the present study because of its well-known kinetic and thermodynamic stability and because of the nature of the d^3 isotropic electronic ground state which makes the interpretation of the NMR of its solutions less complicated. The changes in carbon-13 and hydrogen-1 chemical shifts upon addition of the $Cr(acac)_3$ are reported for the solvents.

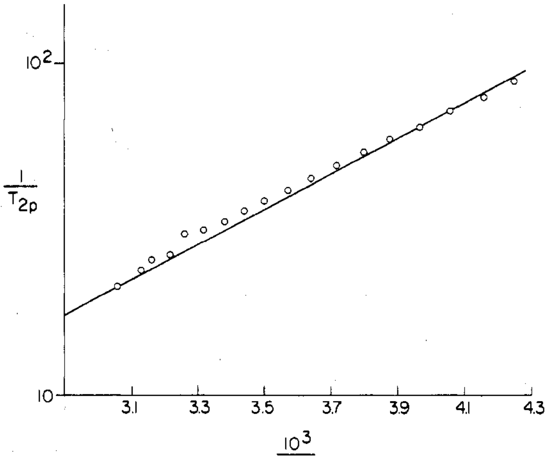

Figure 1. Line broadening of the methyl protons of acetonitrile for 0.1 M $Cr(acac)_3$ in acetonitrile.

Experimental Section

Proton line broadening and chemical shift measurements and carbon-13 chemical shift and T_1 measurements were made on each of the four solvents, benzene, acetonitrile, methanol, and dimethyl sulfoxide (DMSO), in the absence and presence of $Cr(acac)_3$. Data resulting from the temperature dependence of the proton line broadening were analyzed using the methods of Swift and Connick.[14] All data were normalized to 0.1 M $Cr(acac)_3$ where the concentration of $Cr(acac)_3$ ranged from 0.05 to 0.1 M. The proton NMR data were obtained using Varian A-60A and EM-390 spectrometers. The carbon-13 data were obtained using a Bruker HX-90 FT spectrometer with a Nicolet 1085 data system. TMS was used as an internal reference for the chemical shift studies.

All solvents were of spectrochemical quality. The $Cr(acac)_3$, obtained commercially, was purified by recrystallization.

Results and Discussion

Figure 1 shows a Swift–Connick plot for $Cr(acac)_3$ in acetonitrile. The results for acetonitrile are also typical of the results for benzene and DMSO. The plot is linear with positive slope; $\Delta H^{\ddagger}$ for the single process observed is 2.44 kcal/mol. From the temperature dependence of the relaxation rate, T_{2p}^{-1}, and the value of $\Delta H^{\ddagger}$, exchange is fast as defined by the Swift–Connick relationship.[14] In the fast-exchange region, the Swift–Connick equation reduces to $1/T_{2p} = f/T_{2m}$, where f