stabilization of the π-bonding $e_g(xz, yz)$ and $b_{2g}(xy)$ orbitals with respect to the nearly nonbonding or weakly σ-antibonding $a_{1g}(z^2)$ orbital is consistent with the π-acceptor character of the P-donor, CO, or CN^- ligands.

It is interesting that the energies of the MLCT excited states for a given metal ion depend upon the number of acceptor ligands in the complex. For example, among the Ir(I) complexes the energy of the lowest energy MLCT state decreases in the order $[IrX_2(CO)_2]^-$ (X^- = Cl^- or Br^-; two acceptor ligands) > *trans*-$[IrCl(CO)(PPh_3)_2]$ (three acceptor ligands) > $[Ir(CNC_2H_5)_4]^+$ ~ $[Ir(CN)_2(CO)_2]^-$ ~ $[Ir(Ph_2CHCHPPh_2)_2]^+$ ~ $[Ir(Ph_2PCH_2CH_2PPh_2)_2]^+$ (four acceptor ligands). This trend, though not large, is consistent with stabilization of the lowest energy empty MO (a_{2u} in Figure 4) as additional acceptor ligands are added. In contrast, the π-donor properties of the ligands appear to have little effect on the MLCT spectra. There is almost no difference in the spectra of the $[MX_2(CO)_2]^-$ ions for X^- = Cl^- or Br^-. Further, there is very little difference between the spectral pattern observed for the $[Ir(CN)_2(CO)_2]^-$ anion and the $[Ir(Ph_2PCHCHPPh_2)_2]^+$ cation. Since there are no filled π orbitals on the P-donor ligands, this similarity indicates that the filled π orbitals of CN^- or CO have little effect on the stability of the $e_g(xz, yz)$ or $b_{2g}(xy)$ occupied metal π orbitals.

Acknowledgment. We thank the National Science Foundation for partial support of this research.

Registry No. $[Rh(Ph_2PCHCHPPh_2)_2]Cl$, 22754-44-5; $[Ir(Ph_2PCHCHPPh_2)_2]Cl$, 36390-37-1; $[Rh(Ph_2PCH_2CH_2PPh_2)_2]Cl$, 15043-47-7; $[Ir(Ph_2PCH_2CH_2PPh_2)_2]Cl$, 15390-38-2; *trans*-$[RhCl(CO)(PPh_3)_2]$, 15318-33-9; *trans*-$[IrCl(CO)(PPh_3)_2]$, 15318-31-7; $[(n\text{-}C_4H_9)_4N][RhCl_2(CO)_2]$, 17966-76-6; $[(n\text{-}C_4H_9)_4N][IrCl_2(CO)_2]$, 53993-19-4; $[(n\text{-}C_4H_9)_4N][RhBr_2(CO)_2]$, 30191-99-2; $[(n\text{-}C_4H_9)_4N][IrBr_2(CO)_2]$, 62637-68-7; $[Ir(CN)_2(CO)_2]^-$, 62637-67-6.

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Synthesis and Characterization of Cobalt(II) Halide and Pseudohalide Complexes of 4-*N*,*N*-Dimethylaminopyridine

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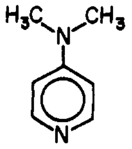
Received January 21, 1977 AIC700547

Six new halide and pseudohalide complexes of Co(II) with 4-*N*,*N*-dimethylaminopyridine (4-DMAP) have been prepared and are of the type $Co(4\text{-}DMAP)_2X_2$ (X is Cl, Br, I, NCO, NCS, or NCSe). Shifts which occur upon complexation of bands in the 1600–1800-cm^{-1} region, assigned to 4-DMAP nucleus stretching modes, confirm that the pyridine nitrogen is coordinated. The pseudohalides are N bonded to Co as evidenced by their ν_{CN} integrated absorption coefficients of approximately 1.2×10^5 M^{-1} cm^{-2}. In the temperature range 300–78 K the halide complexes are magnetically normal (4.6 μ_B at 300 K) whereas the pseudohalide complexes are magnetically subnormal (4.0 μ_B at 300 K). Ligand field spectra of the complexes are typical of C_{2v} Co(II) complexes and show the normal spectrochemical series for *Dq*. On the basis of the values of *Ds* calculated from a C_{2v} model the complexes exhibit increasing distortion from T_d symmetry in the series *N*CO < I < Br < *N*CS ~ Cl < *N*CSe. The presence of the strongly electron-donating 4-dimethylamino group does not markedly affect the electronic and structural properties of these complexes.

Introduction

A very large number of pseudotetrahedral complexes of chromophoric type CoN_2X_2 containing pyridine or its derivatives have been prepared and characterized.[1] In many cases variations in the electronic properties of a series of such complexes have been interpreted in terms of steric and electronic characteristics of the pyridine substituent. For example Haigh et al.[2] have related the metal–pyridine nitrogen stretching frequency of a series of substituted pyridine complexes to the electron-withdrawing ability of the substitutent. Also Nathan and Ragsdale[3] have related N–O stretching frequencies of a series of substituted pyridine *N*-oxides to their respective substituent constants, σ_{pyO}.[4] To study the effect of substitution on electronic properties of complexes containing pyridine substituted with groups capable of conjugation with the ring we have prepared and characterized the cobalt(II) halide and pseudohalide complexes of the strong base 4-*N*,*N*-dimethylaminopyridine (4-DMAP, I).



I

Herein we report results of this work and observe that the presence of this particular substituent does not markedly affect the properties of these complexes but rather their electronic and structural properties are similar to other C_{2v} Co(II) complexes.[5]

Experimental Section

Materials. 4-*N*,*N*-Dimethylaminopyridine was purchased from Aldrich Chemical Co. and used without purification. $CoCl_2 \cdot 6H_2O$, $Co(NCS)_2$, and $CoBr_2$ were purchased from Ventron Corp. and used as received. CoI_2 was prepared from concentrated HI and $CoCO_3$.

Table II. Magnetic Susceptibility Data[a]

X	$-\chi^c$, cgsu	*T*, K	$\chi_M{}^c$, cgsu	μ_{eff}, μ_B
Cl	175	298.2	8 960	4.62
		78.0	31 960	4.46
Br	197	293.3	8 300	4.41
		78.0	28 200	4.20
I	229	294.9	8 800	4.56
		78.0	30 000	4.33
NCO	189	295.1	7 380	4.17
		78.0	26 800	4.06
NCS	190	295.1	6 700	3.98
		78.0	24 600	3.91
NCSe	190	295.5	6 900	4.04
		78.0	25 400	3.98

[a] Uncorrected for TIP.

Table III. Pyridine Nucleus Stretching Frequencies[a]

Compd	ν_{CC}, ν_{CN}				
	A_g	B_{1g}	B_{2u}	B_{3u}	$\nu_{C-N(CH_3)_2}$
4-DMAP[c]	1603	1542	1523	1445	1378
$Co(4\text{-}DMAP)_2Cl_2$[b]	1620	1547	1531	1443	1395
$Co(4\text{-}DMAP)_2Br_2$[b]	1620	1545	1531	1443	1398
$Co(4\text{-}DMAP)_2I_2 \cdot {}^1/_2H_2O$[b]	1620	1543	1531	1442	1397
$Co(4\text{-}DMAP)_2(NCO)_2$[c]	1619		1542	1450	1393
$Co(4\text{-}DMAP)_2(NCS)_2$[c]	1621		1548	1449	1396
$CO(4\text{-}DMAP)_2(NCSe)_2$[c]	1621		1540	1449	1396

[a] Values in cm^{-1}. [b] KBr pressed pellets. [c] Chloroform solution.

All solvents used in spectral studies were spectral grade.

$Co(4\text{-}DMAP)_2Cl_2$. Dichlorobis(4-*N*,*N*-dimethylaminopyridine)cobalt(II) was prepared by adding a warm methanol solution of 2.37 g (10 mmol) of $CoCl_2 \cdot 6H_2O$ to a solution of 2.24 g (20 mmol) of 4-DMAP in hot methanol containing approximately 5% by weight of 2,2-dimethoxypropane. The resulting blue solution was cooled to 0 °C whereupon deep blue crystals separated after several hours. The product, when collected, was washed with cold methanol and dried in vacuo at room temperature. Anal. Calcd for $CoC_{14}H_{20}N_4Cl_2$: C, 44.94; H, 5.39; N, 12.30; Cl, 18.95. Found: C, 45.02; H, 5.41; N, 12.24; Cl, 18.90; mp 230–235 °C (uncor).

$Co(4\text{-}DMAP)_2Br_2$. Dibromobis(4-*N*,*N*-dimethylaminopyridine)cobalt(II) was prepared in the same manner as $Co(4\text{-}DMAP)_2Cl_2$ by using ethanol as solvent. Anal. Calcd for $CoC_{14}H_{20}N_4Br_2$: C, 36.31; H, 4.35; N, 12.10; Br, 34.51. Found: C, 36.64; H, 4.65; N, 11.95; Br, 34.49; mp 249–251 °C (uncor).

$Co(4\text{-}DMAP)_2I_2 \cdot {}^1/_2H_2O$. Diiodobis(4-*N*,*N*-dimethylaminopyridine)cobalt(II) hemihydrate was prepared in the same manner as the bromide complex. The blue product was twice recrystallized from hot ethanol. Anal. Calcd for $CoC_{14}H_{20}N_4I_2 \cdot {}^1/_2H_2O$: C, 29.70; H, 3.56; N, 9.90; I, 44.84. Found: C, 29.35; H, 3.74; N, 9.85; I, 44.83; mp 180–189 °C (uncor).

$Co(4\text{-}DMAP)_2(NCO)_2$. Diisocyanatobis(4-*N*,*N*-dimethylaminopyridine)cobalt(II) was prepared by using the following two-phase method. An aqueous solution of 1.46 g (4 mmol) of $Co(ClO_4)_2 \cdot 6H_2O$ was slowly added to a solution of 0.65 g (8 mmol) of KOCN dissolved in the minimum amount of water. The resulting blue solution was extracted with 10 mL of CH_2Cl_2 containing 0.92 g (7.5 mmol) of 4-DMAP. The blue organic phase was evaporated nearly to dryness and the resulting blue precipitate was recrystallized from benzene. Anal. Calcd for $CoC_{16}H_{20}N_6O_2$: C, 49.62; H, 5.20; N, 21.70. Found: C, 49.38; H, 5.15; N, 21.46; mp 130 °C (uncor).

$Co(4\text{-}DMAP)_2(NCS)_2$. Diisothiocyanatobis(4-*N*,*N*-dimethylaminopyridine)cobalt(II) was prepared by dissolving stoichiometric amounts of $Co(SCN)_2$ and 4-DMAP in absolute ethanol and heating to 40–50 °C for 30 min. The resulting deep blue solution was cooled to room temperature and the blue crystalline product once collected was washed with cold ethanol and air-dried at room temperature. Anal. Calcd for $CoC_{16}H_{20}N_6S_2$: C, 45.82; H, 4.81; N, 20.04; S, 15.29. Found: C, 45.59; H, 4.86; N, 19.80; S, 15.32; mp 160–165 °C (uncor).

$Co(4\text{-}DMAP)_2(NCSe)_2$. Diisoselenocyanatobis(4-*N*,*N*-dimethylaminopyridine)cobalt(II) was prepared in the same manner as the isocyanate complex by using $Co(ClO_4)_2 \cdot 6H_2O$ and KSeCN. The product was repeatedly washed with warm benzene to remove traces of uncomplexed 4-DMAP. Anal. Calcd for $CoC_{16}H_{20}N_6Se_2$: C, 37.45; H, 3.93; N, 16.37; Se, 30.64. Found: C, 37.40; H, 3.92; N, 16.40; Se, 30.74; mp 130 °C (uncor).

Analytical Methods. Halides were determined by Volhard titration with $Fe(NH_4)(SO_4) \cdot 12H_2O$ as indicator. C, H, N, S, and Se were analyzed by Galbraith Laboratories, Knoxville, Tenn.

Physical Measurements. X-ray powder patterns were obtained by using the Straumanis technique with nickel-filtered Cu Kα radiation (λ_{mean} 1.5417 Å). *d* spacings and apparent intensities are given in Table I.[6] Magnetic susceptibilities were determined on polycrystalline samples at ambient and liquid nitrogen temperatures by using a standard Gouy balance calibrated with $HgCo(NCS)_4$. Diamagnetic corrections for the ligands were obtained from a table of Pascal's constants.[7] Electronic spectra were recorded on a Cary 14 by using an Air Products AC-2 Cryo-Tip refrigerator operating on a hydrogen cycle (23 K). Infrared spectra were recorded on a Perkin-Elmer 180 instrument calibrated with polystryene and are reproducible to 1 cm^{-1}. Integrated absorption coefficients were obtained by using the equations of Ramsay.[8]

Results

The complexes prepared in this study are stable in the solid state and in solution. The pseudohalide complexes are soluble in a range of organic solvents but decompose in water. The halide complexes are only slightly soluble in organic solvents. All the complexes are light insensitive and heat stable. Magnetic susceptibilities obtained at room and liquid nitrogen temperatures are given in Table II. Magnetic moments reported in Table II are average values for two separate preparations and their estimated uncertainty is approximately 0.03 μ_B.

The integrated absorption coefficient for the C≡N stretching band of each pseudohalide complex dissolved in CH_2Cl_2 was determined by using the direct solution of Ramsay.[8] In each instance this band displayed a shoulder which was separated from the main band by a derivative deconvolution technique.[9] The result for each complex is given as follows (wavenumber, cm^{-1}, followed by absorption coefficient, $A_{CN} \times 10^{-4}$ M^{-1} cm^{-2}): NCO (2209, 13.2), NCS (2068, 13.4), and NCSe (2070, 11.9). The only other bands observed in the IR spectrum which could be assigned to pseudohalide modes were the C–O stretch at 1342 cm^{-1} and the NCO deformation at 614 cm^{-1}.

4-DMAP nucleus stretching frequencies in the 1600–1300-cm^{-1} region and appropriate assignments for these bands are given in Table III. Assignments given here are based on those of Katritzky and Gardner[10] for 4-DMAP. Table IV contains pertinent deformation modes observed in the 800–

Table IV. Low-Frequency Infrared Absorptions[a]

Compd	$\nu_{Co-(4\text{-}DMAP)}$	ν_{Co-X}	$\delta_{C-N(CH_3)_2}$	δ_{ring}
4-DMAP			752	255
$Co(4\text{-}DMAP)_2Cl_2$	240	335, 306	761	280
$Co(4\text{-}DMAP)_2Br_2$	240	285 sh, 260	762	285
$Co(4\text{-}DMAP)_2I_2 \cdot {}^1/_2H_2O$	243		761	280
$Co(4\text{-}DMAP)_2(NCO)_2$	240	370, 330	764	280
$Co(4\text{-}DMAP)_2(NCS)_2$	240	325	762	280
$Co(4\text{-}DMAP)_2(NCSe)_2$	243		763	280

[a] Values in cm^{-1}. Obtained in Nujol on polyethylene.

Table V. Ligand Field Spectral Data[a]

Compd	$^4A_2 \rightarrow {}^4T_1(^4F)$	$^4A_2 \rightarrow {}^4T_1(^4P)$
$Co(4\text{-}DMAP)_2Cl_2$	6100, 7080, 9460	15 450, 15 920, 16 780
$B = 724$	$Dq^{tet} = 370$	$Ds = 335$
$Co(4\text{-}DMAP)_2Br_2$	6200, 7340, 9500	15 380, 16 080, 16 750
$B = 724$	$Dq^{tet} = 370$	$Ds = 500$
$Co(4\text{-}DMAP)_2I_2 \cdot {}^1/_2H_2O$	6020, 7020, 8900	14 490, 15 270, 16 130
$B = 669$	$Dq^{tet} = 360$	$Ds = 557$
$Co(4\text{-}DMAP)_2(NCO)_2$	6900, 7840, 9900	16 200, 17 000, 18 100
$B = 735$	$Dq^{tet} = 410$	$Ds = 571$
$Co(4\text{-}DMAP)_2(NCS)_2$	7250, 8200, 10 000	16 470, 16 950, 17 700
$B = 735$	$Dq^{tet} = 430$	$Ds = 342$
$Co(4\text{-}DMAP)_2(NCSe)_2$	7520, 8330, 9800	16 470, 16 870, 17 860
$B = 724$	$Dq^{tet} = 450$	$Ds = 285$

[a] Values in cm^{-1}. KBr pressed pellets at 23 K. *Ds* values based on the model of Flamini et al.[22]

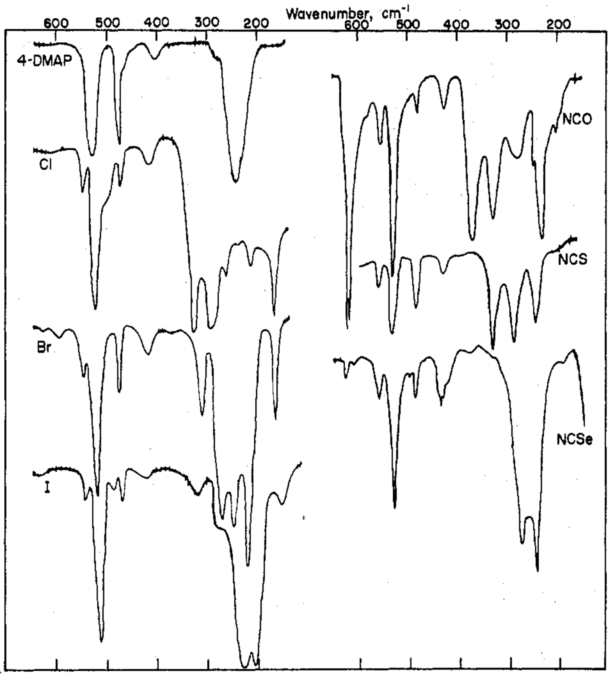


Figure 1. Low-frequency (700–150 cm^{-1}) spectrum of 4-DMAP and its cobalt(II) halide and pseudohalide complexes.

200-cm^{-1} region, metal–ligand stretching frequencies, and appropriate assignments. Figure 1 shows the low-frequency spectrum of 4-DMAP and its Co(II) complexes.

Ligand field band positions, assignments, and parameters obtained at 23 K are given in Table V. In all cases the room-temperature and 23-K band maxima agree within experimental error (100–200 cm^{-1}). Individual component bands of the two observed ligand field absorptions are more clearly resolved in the 23-K spectra than in the room-temperature spectra. The ν_1 band was not observed and no attempt was made to deconvolute the ν_2 and ν_3 envelopes. Solid-state and solution ligand field spectra are similar for each complex.

Discussion

4-DMAP is characterized by its high apparent pK_a of 9.71[11] and dipole moment of 4.40 μ_D (dioxane).[12] The ability of the lone pair of electrons on the dimethylamino group to conjugate with the pyridine ring is most likely responsible for this high pK_a.[11] Furthermore the high dipole moment of 4-DMAP relative to pyridine (2.20 μ_D, dioxane)[12] may be ascribed to this conjugation. Conjugation places a partial positive charge on the aliphatic nitrogen and a partial negative charge on the pyridine nitrogen. Presence of the partial positive charge on the exocyclic nitrogen effectively eliminates this potentially strongly coordinating group from participating in coordination relative to the pyridine nitrogen. A similar argument was employed[13] to explain the relative reactivities of 2-, 3-, and 4-DMAP toward methylation and *N*-oxide formation. Whereas methylation and *N*-oxide formation of 2-DMAP occurred at the exocyclic nitrogen, the same reactions of 4-DMAP occurred at the ring nitrogen.[13]

Room-temperature magnetic moments of these complexes (Table II) are in the range predicted for C_{2v} Co(II) complexes (4.70–3.87 μ_B).[14] In addition, the moments decrease with decreasing temperature as expected. Moments of the pseudohalides are very close to the spin-only moment, μ_{so}. This indicates that orbital contribution to the moment has been almost totally quenched. Possible causes of this quenching are low-symmetry ligand field and/or covalency effects. It is possible to approximate the orbital reduction (covalency) factor, *k*, for each of these complexes by using expression 1

$$k = \left[\frac{10Dq}{4\lambda_0}\left(1 - \frac{\mu_{eff}}{\mu_{so}}\right)\right]^{1/2} \tag{1}$$

which is appropriate for an A_2 term. In eq 1 λ_0 is the free-ion spin–orbit coupling constant (−175 cm^{-1} for Co^{2+}). By using μ_{eff} values given in Table II and *Dq* values in Table V the following values of *k* may be calculated: Cl, 1.00; Br, 0.86; I, 0.96; NCO, 0.67; NCS, 0.42; NCSe, 0.53. Because it is not possible at this stage to assess the importance of the mixing-in of excited state t_2 with ground-state e wave functions, the value of the covalency factor may be in considerable error for any one of these complexes. Nonetheless we believe that the pseudohalide complexes are more covalent than the halide complexes because of the rather large difference between these two sets of covalency parameters. This greater covalency is expected because pseudohalides are better σ donors than halides.

Upon complexation all three of the absorptions assigned to C=C and C=N ring stretching modes shift to higher wavenumber (Table III). Shift of the A_g mode (approximately 17 cm^{-1}) is insensitive to X. The B_{2u} mode, which contains a good deal of C=N stretching character, shifts 8 cm^{-1} for the halide complexes, approximately 18 cm^{-1} for the NCO and NCSe complexes, and 25 cm^{-1} for the NCS complex. This is the inverse order of the covalency factors given above. Such an inverse correlation is expected because, as the σ-donor capability of X increases, the positive charge on the cobalt ion decreases thereby decreasing the strength of the Co–4-DMAP bond. Although it appears that a similar correlation exists for the B_{1g} mode, our limited data do not allow such an analysis. (The B_{1g} and B_{2u} modes coalesce in the pseudohalide complexes.) Because it is not appropriate to speak of π-acceptor capabilities in tetrahedral complexes,[15] it would be instructive to prepare and characterize the $(4\text{-}DMAP)_4Co^{II}X_2$ octahedral complexes. We have not thus far observed the formation of these tetrakis complexes.

Metal–ligand stretching frequencies reported in Table IV are similar to those reported for other C_{2v} Co(II) complexes of substituted pyridine ligands.[16] A total of four IR-active modes are expected for C_{2v} complexes but frequently fewer are observed.[17] We find an X-insensitive band at approximately 240 cm^{-1} (Figure 1) which we have assigned to $\nu_{\text{Co-(4-DMAP)}}$ and two bands (Table IV) for the Cl and Br complexes which are assigned to $\nu_{\text{Co-Cl}}$ and $\nu_{\text{Co-Br}}$. We have not resolved $\nu_{\text{Co-I}}$ or $\nu_{\text{Co-NCSe}}$ absorptions from the low-frequency ligand bands (Figure 1). Assignments for $\nu_{\text{Co-NCO}}$ and $\nu_{\text{Co-NCS}}$ have also been made at 370 and 330 and 325 cm^{-1}, respectively.

Ligand field spectral data given in Table V are rather typical of CoN_2X_2 complexes.[1] Two absorptions are observed. The first, in the near-infrared region centered at approximately 7500–8500 cm^{-1} is assigned to the $^4A_2 \rightarrow {}^4T_1(^4F)$, ν_2, transition and the second, centered at approximately 16 000 cm^{-1} is assigned to the $^4A_2 \rightarrow {}^4T_1(^4P)$, ν_3, transition. By using the crystal field matrix elements of König[19] and by weighting the individual components of the bands according to their spin–orbit coupling energies, we have calculated values for the tetrahedral crystal field splitting parameters Dq^{tet} and B. The series of Dq^{tet} values follows the classical spectrochemical series NCSe > NCS > NCO > Cl ~Br > I. Because the overall splitting of ν_2 and ν_3 is considerably larger than $6\lambda_0$,[20] we have calculated the second-order distortion parameter Ds[21] by using the electrostatic matrix elements given by Flamini et al.[22] These values of Ds decrease in the order NCO > I > Br > NCS ~ Cl > NCSe. The fact that this series does not correlate with the normal spectrochemical series may indicate that the model[22] used to calculate Ds is inadequate for these complexes.

Conclusion

We have determined that 4-DMAP forms pseudotetrahedral complexes with Co(II) halides and pseudohalides and have concluded that these compounds are similar to other C_{2v} Co(II) complexes containing substituted pyridine ligands. Future investigations are planned to obtain the mass spectral fragmentation patterns and ^{13}C NMR spectra of these complexes. In addition we are planning a study of the corresponding 2-DMAP and 3-DMAP complexes.

Registry No. $Co(4\text{-DMAP})_2Cl_2$, 62660-95-1; $Co(4\text{-DMAP})_2Br_2$, 62882-88-6; $Co(4\text{-DMAP})_2I_2$, 62882-87-5; $Co(4\text{-DMAP})_2(NCO)_2$, 62882-86-4; $Co(4\text{-DMAP})_2(NCS)_2$, 62882-85-3; $Co(4\text{-DMAP})_2(NCSe)_2$, 62882-84-2; 4-DMAP, 1122-58-3.

Supplementary Material Available: A listing of the x-ray powder diffraction *d* spacings, Table I (2 pages). Ordering information is given on any current masthead page.

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Hydrolysis Kinetics of (–)-Sparteine–Copper(II) Halides[1a–c]

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Received January 28, 1977 AIC700749

The hydrolysis kinetics of the reactions of (–)-sparteine–copper(II) chloride and (–)-sparteine–copper(II) bromide were studied to determine a possible mechanism for the process. Of particular interest were the slowness of the reaction and the catalytic effect of halide ions on the hydrolysis reaction. The parameters investigated were concentration, temperature, and halide concentration, which have positive effects on the rate, and the pH and ionic strength, which have minimal effects. The results suggest a mechanism in which the rate-determining step is a conformational inversion from a cisoid to a transoid form of the sparteine moiety followed by a subsequent attack by water or a halide ion. The reactions proceed according to the rate law $-d[C_{15}H_{26}N_2\cdot CuX_2]/dt = [(k_1k_2 + k_1k_3X)/(k_{-1} + k_2 + k_3X)][C_{15}H_{26}N_2\cdot CuX_2]$. From measurements over the 25–55 °C temperature range the $\Delta H^{\ddagger}$ values are found to be 16.0 and 23.1 kcal/mol, and the $\Delta S^{\ddagger}$ values are –24.4 and –1.45 eu, for the chloro and bromo complexes, respectively. The difference in kinetic behavior is explained in terms of halide size differences and the nucleophilicity differences of the halide ions.

Introduction

Recently there has been increased interest in the chemistry of sparteine alkaloids, $C_{15}H_{26}N_2$, and their metal salt adducts.[2-11] Particular interest in the chemistry of these alkaloids has arisen because of their biological and physiological use in the stimulation of muscular action in the heart, lung, and uterus.[12] Since the ions of metals such as calcium[13a] and magnesium[13b] appear to play a sensitive role in muscle activity, the complex formation process may affect in some manner the equilibria or kinetic processes involving these metal ions.[14] To provide additional information for understanding and elucidating the detailed mechanism of this effect as well as ex-