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Circular Dichroism Spectra of Cobalt(III) and Platinum(II) Complexes of the *tert*-Butyl-Substituted Diamine 3,3-Dimethyl-1,2-butanediamine

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The *tert*-butyl-substituted diamine (*S*)-3,3-dimethyl-1,2-butanediamine (dmbn) forms five-membered chelate rings with metals that are effectively restricted to the δ conformation in which the *tert*-butyl group is equatorial. The absorption and circular dichroism spectra are reported for $[Co(NH_3)_4((S)\text{-dmbn})]^{3+}$, $[Co(CN)_4((S)\text{-dmbn})]^-$, *trans*-$[CoCl_2((S)\text{-dmbn})_2]^+$, Λ-$[Co((S)\text{-dmbn})_3]^{3+}$, and $[Pt(NH_3)_2((S)\text{-dmbn})]^{2+}$. The spectra are compared to those for other monosubstituted diamines 1,2-propanediamine (pn) and 1-phenyl-1,2-ethanediamine, and it is concluded that in $[Pt(NH_3)_2((S)\text{-pn})]^{2+}$ the δ conformation is 70% populated. The effect of solvation on the spectra is examined, and on the basis of the results of ^1H NMR spectroscopy of the complexes, the changes in the circular dichroism with solvent are interpreted in terms of the creation of asymmetric nitrogen donors via the stereoselective solvation of the NH_2 protons. The bulky *tert*-butyl group is found to limit solvation at the adjacent NH_2 compared to the analogous methyl derivative. The ^{13}C NMR spectra show no evidence that more than one geometrical isomer of *trans*-$[CoCl_2((S)\text{-dmbn})_2]^+$ and Λ-$[Co((S)\text{-dmbn})_3]^{3+}$ is present, and the spectrum of the latter complex is consistent with the facial structure. The ^{59}Co spectrum of the tris complex confirms the presence of only one isomer.

Introduction

The circular dichroism (CD) induced in the d–d transitions of metal complexes containing chiral chelate ligands is commonly factorized into three contributions: the configurational effect due to a dissymmetric arrangement of chelate rings about the metal, the conformational effect caused by puckered dissymmetric conformations of the individual chelate rings, and the vicinal effect due to asymmetric groupings in the ligands.[1] For mono and trans bis complexes with chiral bidentate chelates, the configurational effect is not relevant; where the chelate is a five-membered diamine, the CD is believed to derive mainly from the conformational effect,[1-3] although in phenyl-substituted diamines a vicinal effect appears to be significant.[3,4]

Investigation of the conformational effect requires a knowledge of the mole fractions of the various populated conformers. For five-membered diamine chelate rings there are two chiral conformers, δ and λ, which have the substituent in equatorial and axial orientations, respectively, for alkyl- or aryl-substituted diamines with the *S* configuration.[5] The investigation is simplified if the chelate adopts one conformation exclusively. Complexes of the *tert*-butyl substituted diamine 3,3-dimethyl-1,2-butanediamine, which has been given the abbreviation dmbn,[6] are of special interest as it has been shown that the *S* isomer effectively adopts the δ conformer exclusively in octahedral and square-planar complexes (Figure 1).[6,7] The CD of some mono and *trans*-bis((*S*)-3,3-dimethyl-1,2-butanediamine) complexes of cobalt(III) and platinum(II) are reported here and are compared with the CD of related complexes with other monosubstituted diamines.

The solvent has been observed to have a major influence on the CD of some related complexes.[2,8] For *trans*-dihalobis((*R*)-1,2-propanediamine)cobalt(III) it has been shown that the solvent exerts its influence primarily through stereoselective hydrogen-bond interactions with the NH_2 groups of the diamine chelates.[8] The effect of the bulky *tert*-butyl group on this solvation is investigated in this paper.

The study of the CD of tris(diamine)cobalt(III) complexes has had a very important role in the development of the field of metal complex optical activity.[1,9-14] In these complexes the configurational effect is usually dominant. In the present paper, the preparation and CD of Λ-$[Co((S)\text{-dmbn})_3]^{3+}$ are reported. Carbon-13 NMR is used to study which geometrical isomer was prepared and for this complex and *trans*-$[CoCl_2((S)\text{-dmbn})_2]^+$ to determine the isomeric purity of the complexes. Cobalt-59 NMR, which is particularly sensitive to structural changes, is used to confirm the number of stereoisomers present in the tris complex.

Experimental Section

Materials. 3,3-Dimethyl-1,2-butanediamine was prepared and resolved by a published procedure.[6] However, better resolution was achieved with $[\alpha]_D^{293}$ +44.0° (*c* 1.0, benzene) (literature 32.15°).[6] The absolute configuration of this isomer has been shown to be *S* by an X-ray study of salts of its tetraamminecobalt(III) complex.[7] Potassium tetracyano((*S*)-3,3-dimethyl-1,2-butanediamine)cobaltate(III) was prepared by a published method.[6] All other reagents were of AnalaR grade. The solvents used for spectroscopy were dried and distilled by standard methods. Microanalyses were carried out by the University of Queensland's microanalytical service.

Preparation of Tetraammine((*S*)-3,3-dimethyl-1,2-butanediamine)cobalt(III) Nitrate Sesquihydrate. The complex was prepared by the general method of Yoneda and co-workers[15] and was recrystallized from dilute nitric acid. Anal. Calcd for $C_6H_{31}N_9CoO_{10.5}$: C, 15.8; H, 6.8; N, 27.6. Found: C, 15.9; H, 6.6; N, 27.7. An attempt was made to isolate the perchlorate salt of the complex by adding several drops of concentrated perchloric acid to a filtered, concentrated solution of the nitrate salt. The crystals that precipitated on cooling analyzed as the mixed nitrate perchlorate salt $[Co(NH_3)_4((S)\text{-dmbn})](NO_3)_{1.5}(ClO_4)_{1.5}$. Anal. Calcd for $C_6H_{28}CoCl_{1.5}N_{7.5}O_{10.5}$:

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(5) For simplicity of discussion, only the *S* isomer of diamines will be considered even though in a number of the references cited the *R* isomer has been used and the CD spectra published are for the *R* isomer. Where this has occurred, the CD has been inverted.

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Figure 1. δ conformation for the chelate ring formed by (*S*)-3,3-dimethyl-1,2-butanediamine with X equal to $C(CH_3)_3$.

C, 14.9; H, 5.8; N, 21.6. Found: C, 15.0; H, 5.5; N, 22.0. A similar mixed salt has been reported for the analogous complex of (*R*)-phenyl-1,2-ethanediamine.[4]

Preparation of *trans*-Dichlorobis((*S*)-3,3-dimethyl-1,2-butanediamine)cobalt(III) Perchlorate. The chloride salt of the complex was prepared by the method for the corresponding 1,2-propanediamine complex.[16] It was converted to its perchlorate salt by precipitation from a methanolic solution with perchloric acid. Anal. Calcd for $C_{12}H_{32}CoCl_3N_4O_4$: C, 31.2; H, 7.0; Cl, 23.0; N, 12.1. Found: C, 31.0; H, 6.9; Cl, 23.2; N, 12.1. For spectroscopic studies in acetonitrile, the tetraphenylborate salt was freshly prepared by the addition of a filtered, concentrated, aqueous solution of sodium tetraphenylborate to a solution of the perchlorate in dilute perchloric acid. The mixture was stirred for 30 min and filtered to yield a pale greeen product, which was dried under vacuum over P_2O_5.

Preparation of Λ-Tris((*S*)-3,3-dimethyl-1,2-butanediamine)cobalt(III) Chloride Hydrate. The method of Krause and Megargle[17] for $[Co(en)_3]^{3+}$ was used to prepare $[Co((S)\text{-dmbn})_3]Cl_3{\cdot}H_2O$. Anal. Calcd for $C_{18}H_{50}CoCl_3N_6O$: C, 40.6; H, 9.5; N, 15.8. Found: C, 40.9; H, 9.2; N, 15.6. Column chromatography using a procedure published previously for $[Co(pn)_3]^{3+}$ [11] and ^1H, ^{13}C, and ^{59}Co NMR spectra of the complex were consistent with only one isomer being present.

Preparation of Λ-Tris((*S*)-3,3-dimethyl-1,2-butanediamine)cobalt(III) Chloride Perchlorate. An alternative method of preparation of the tris complex was also successful. 3,3-Dimethyl-1,2-butanediamine was added in a mole ratio of 3:1 to a solution of *trans*-dichlorotetrakis(pyridine)cobalt(III) chloride[18] in a minimum volume of dry dimethyl sulfoxide. Reaction was immediate with the solution changing from a deep green to a deep orange. On addition of ethanol and ether, an oil was formed, which on trituration with acetone produced an orange solid that was removed by filtration. The solid was dissolved in a minimum volume of warm water, the solution was filtered, and several drops of concentrated perchloric acid were added. The orange crystals that precipitated from the cooled solution were filtered, washed with ice-cold water, and dried under vacuum. The product analyzed as a mixed chloride perchlorate salt. Anal. Calcd for $C_{18}H_{48}CoCl_3N_6O_6$: C, 35.5; H, 7.9; Cl, 17.4; N, 13.8. Found: C, 35.7; H, 8.4; Cl, 17.3; N, 13.7. No evidence for a second isomer was again obtained.

Preparation of Diammine((*S*)-3,3-dimethyl-1,2-butanediamine)platinum(II) Chloride Hydrate. The complex was prepared by the general method of Appleton and Hall.[19] Anal. Calcd for $C_6H_{24}Cl_2N_4OPt$: C, 16.6; H, 5.1; Cl, 16.3; N, 12.9. Found: C, 16.9; H, 5.4; Cl, 16.3; N, 12.5.

Spectroscopy. UV–visible absorption and CD spectra were measured on a Cary 17 spectrophotometer and a Jobin Yvon Mark III Dichrograph, respectively. Specific rotations were measured in a 0.1-m cell with a Perkin-Elmer 141 polarimeter. The ^1H (100 MHz), ^{13}C (25.1 MHz), and ^{59}Co (23.6 MHz) NMR spectra were measured on a JEOL FX100 FT-NMR spectrometer. For the ^1H NMR sodium 3-(trimethylsilyl)propanesulfonate and tetramethylsilane were used as internal references. The ^{13}C NMR spectra were measured in the proton noise-decoupled mode with dioxan (δ 67.4) as the internal reference. Assignments of the ^{13}C resonances were based on off-resonance proton-decoupled spectra. For the ^{59}Co NMR spectra, a ^7Li external lock was used, and $[Co(NH_3)_6]^{3+}$ (δ 0) was used as an external reference.

Results

Absorption and CD Spectra. The absorption and CD spectra are given in Figures 2–6. The CD bands with $^1A_{1g} \rightarrow {}^1T_{1g}$ (O_h) parentage for the dmbn complexes are compared with those of other diamines in Table I.

Table I. CD Data for Bands with $^1A_{1g} \rightarrow {}^1T_{1g}$ (O_h) Parentage for Cobalt(III) Complexes with (*S*)-Diamines

	band I		band II		
diamine	λ, nm	Δϵ	λ, nm	Δϵ	ref
		(i) $[Co(NH_3)_4L]^{3+}$ [a]			
dmbn	526	+0.04	462	−0.39	*b*
pn	517	+0.06	461	−0.34	*c*
pen	528	+0.02	464	−0.17	*d*
		(ii) $[Co(CN)_4L]^-$ [a]			
dmbn	400	+0.12	348	−0.77	*b*
pn	397	+0.15	347	−0.67	*e*
pen			352	−0.44	*d*
		(iii) *trans*-$[CoCl_2L_2]^+$ [f]			
dmbn	612	−0.81	464	+0.15	*b*
pn	602	−0.76	463	+0.10	*g*
	602	−0.82	463	+0.12	*h*
pen	618	−0.52	459	−0.42	*d*
	615	−0.45	465	−0.28	*i*
		(iv) Λ-$[CoL_3]^{3+}$ [a]			
dmbn	499	+2.13	441	−0.58	*b*
pn	493	+1.95	439	−0.58	*j*
	494	+2.12	440	−0.63	*k*
pen	497	+2.68	433	−0.49	*l*

[a] In water. [b] This work. [c] Reference 23. [d] Reference 4. [e] Reference 25. [f] In methanol. [g] Reference 31. [h] Reference 8. [i] Reference 3. [j] Reference 39. [k] Reference 40. [l] Reference 14.

NMR Spectra. The NMR of the $CHCH_2$ protons has been published elsewhere.[7] The NH resonances are of particular relevance to the discussion of the CD spectra and are presented here in Table II for $[Co(CN)_4((S)\text{-dmbn})]^-$ and *trans*-$[CoCl_2((S)\text{-dmbn})_2]^+$. In dimethyl sulfoxide the $N(2)H_{ax}$ resonance for $[Co(NH_3)_4((S)\text{-dmbn})]^{3+}$ occurs at δ 4.32 (t) while the other three NH resonances form a broad band centered at δ 4.94. The solvent peak in 0.01 M D_2SO_4 partially obscures a number of the NH resonances for this complex. The NH resonances were assigned by selective decoupling of the assigned CH resonances. The ^{13}C chemical shift data for the complexes are given in Table III. For each carbon in *trans*-$[CoCl_2((S)\text{-dmbn})_2]^+$ and $[Co((S)\text{-dmbn})_3]^{3+}$ there is no evidence for more than one peak, consistent with isomeric purity. The ^{59}Co chemical shift data (ppm) with half-band-widths in parentheses are as follows: $[Co(NH_3)_4((S)\text{-dmbn})]^{3+}$, −357.2 (195 Hz); $[Co((S)\text{-dmbn})_3]^{3+}$, −818.6 (50 Hz). For the tris complex there was no evidence of a second resonance, again consistent with isomeric purity.

Discussion

Cobalt(III) Complexes. For octahedral cobalt(III) complexes, the spin-paired d^6 configuration gives rise to two spin-allowed transitions in the visible, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$. Both are electric dipole forbidden, but the former is magnetic dipole allowed, and, in the presence of a dissymmetric force field, the low-symmetry components of the former have an induced rotational strength. The complexes $[Co(NH_3)_4((S)\text{-dmbn})]^{3+}$, $[Co(CN)_4((S)\text{-dmbn})]^-$, and *trans*-$[CoCl_2((S)\text{-dmbn})_2]^+$ have tetragonal-holohedrized crystal fields that result in the splitting of the $^1T_{1g}$ level into levels with ^1E_g and $^1A_{2g}$ symmetries and the $^1T_{2g}$ level into levels with ^1E_g and $^1B_{2g}$ symmetries. The separation of the tetragonal components of the $^1A_{1g} \rightarrow {}^1T_{1g}$ absorption is related to the difference in the spectrochemical parameters, Δ, for the ligands.[20,21] The splitting is observed in *trans*-dichlorobis(diamine)cobalt(III), giving rise to absorptions at about 600 and 450 nm that have ^1E_g and $^1A_{2g}$ symmetries, respectively. The splitting is not

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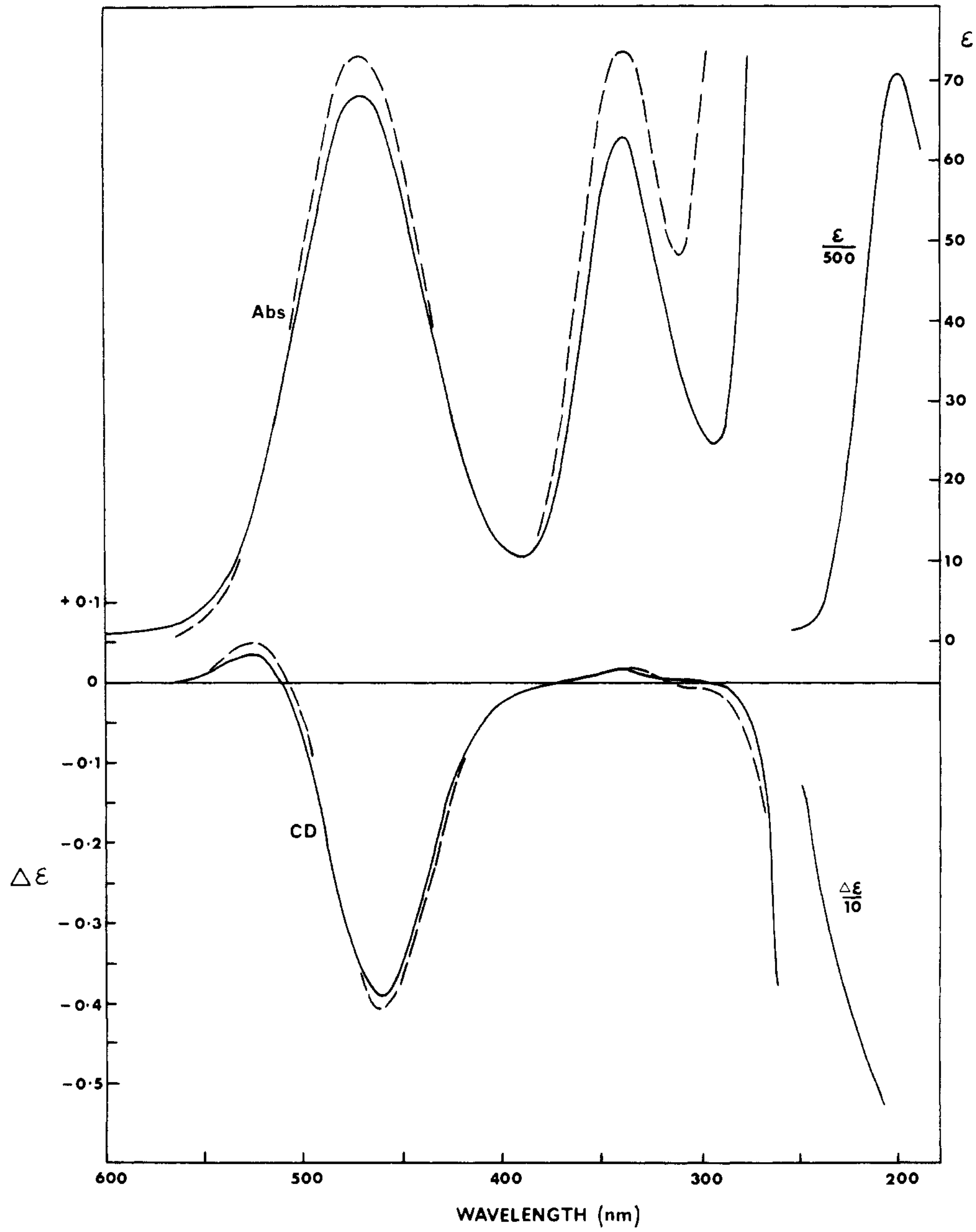

Figure 2. UV–visible absorption and circular dichroism spectra of $[Co(NH_3)_4((S)\text{-dmbn})](ClO_4)_{1.5}(NO_3)_{1.5}$ in water (—) and dimethyl sulfoxide (- - -).

Table II. ^1H Chemical Shift Data for NH Protons[a]

solvent	$N(2)H_{ax}$	$N(2)H_{eq}$	$N(1)H_{ax}$	$N(1)H_{eq}$	$\Delta N(2)$	$\Delta N(1)$	$\Sigma\Delta N$
			(i) $[Co(CN)_4((S)\text{-dmbn})]^-$				
0.01 M D_2SO_4[b]	3.57	4.27	4.29	4.38	0.70	0.09	0.79
CD_3OD[c]	3.39	4.10	4.15	4.25	0.71	0.10	0.81
$(CD_3)_2SO$[b]	3.04	3.49	3.85	4.08	0.45	0.23	0.68
			(ii) $[CoCl_2((S)\text{-dmbn})]^{2+}$				
CD_3CN[c]	4.15	4.68	4.46	4.46	0.53	0	0.53
CD_3OD[c]	4.40	5.37	4.84	5.37	0.97	0.53	1.50
$(CD_3)_2SO$[b]	4.36	5.55	4.83	5.55	1.19	0.72	1.91

[a] N(2) is bound to C(2) and N(1) to C(1). [b] In ppm from sodium 3-(trimethylsilyl)propanesulfonate. [c] In ppm from tetramethylsilane.

observed for the other two complexes, but it has been estimated to be of the order of 100 cm^{-1} or 2 nm for the tetraammine[22] and 1500 cm^{-1} or 19 nm for the tetracyano,[4] with the $^1A_{1g} \rightarrow {}^1E_g$ component lower in energy for the former but higher for the latter. Generally for the tetragonal complexes only one Cotton effect is observed under the $^1A_{1g} \rightarrow {}^1T_{2g}$ absorption, and, as the $^1A_{1g} \rightarrow {}^1B_{2g}$ remains magnetic dipole forbidden under the tetragonal field, this Cotton effect is usually assigned to the $^1A_{1g} \rightarrow {}^1E_g$ component.

For the tris(diamine) complexes it has been established that the trigonal field splits the $^1A_g \rightarrow {}^1T_{1g}$ into two components, $^1A_1$

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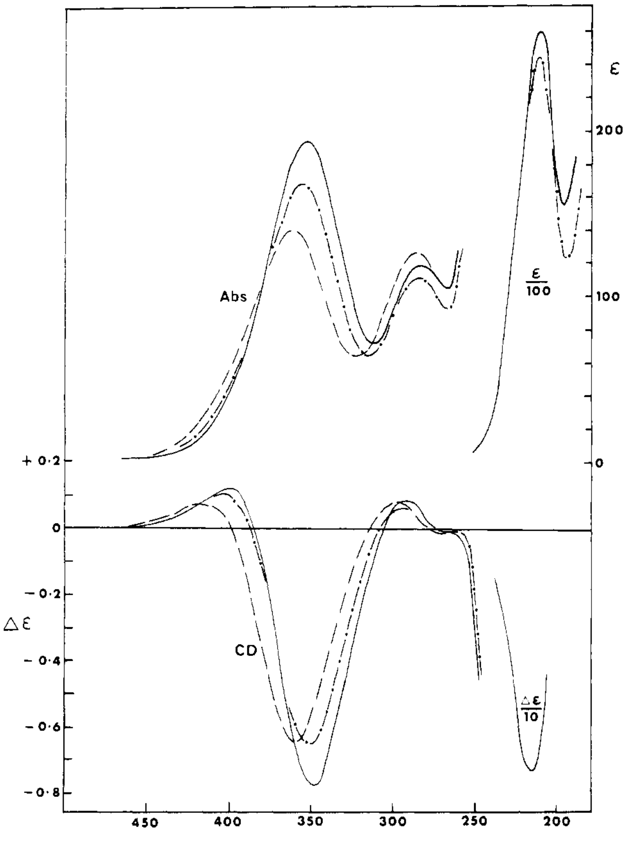

Figure 3. UV–visible absorption and circular dichroism spectra of $K[Co(CN)_4((S)\text{-dmbn})]$ in water (—), methanol (–·–), and dimethyl sulfoxide (---).

Table III. ^{13}C Chemical Shift Data[a] for Complexes of (*S*)-3,3-Dimethyl-1,2-butanediamine

complex	CH	CH_2	C	$(CH_3)_3$
$[Co(NH_3)_4L]^{3+}$ [b]	66.96	46.20	32.94	26.46
$[Co(CN)_4L]^-$ [b]	68.00	47.54	32.96	26.68
trans-$[CoCl_2L_2]^+$ [c]	66.91	46.15	32.70	26.32
$[CoL_3]^{3+}$ [b]	68.13	46.49	32.75	26.61
$[Pt(NH_3)_2L]^{2+}$ [b]	69.54	48.57	32.31[d]	26.73

[a] In ppm from Me_4Si. [b] In D_2O. [c] In CD_3OD. [d] With satellite peaks due to coupling to ^{195}Pt with $^3J_{PtC}$ 41.0 Hz.

→ ^1E and $^1A_1 \rightarrow {}^1A_2$, with the doubly degenerate transition lowest in energy.[1,13]

(i) $[Co(NH_3)_4((S)\text{-dmbn})]^{3+}$. This complex has a CD spectrum very similar to analogous complexes with monosubstituted diamines such as (*S*)-1,2-propanediamine,[23] and (*S*)-1-phenyl-1,2-ethanediamine (pen).[4] The lower energy component of the $^1A_{1g} \rightarrow {}^1T_{1g}$ band is positive and is smaller than the higher energy negative Cotton effect. Under the $^1A_{1g} \rightarrow {}^1T_{2g}$ absorption there is a small positive band, and under the charge-transfer absorption there is a large negative Cotton effect. For the *tert*-butyl[6,7] and phenyl[7,24] derivatives, the chelate ring is exclusively in the δ conformation with the substituent equatorial. For (*S*)-1,2-propanediamine, the λ conformer is slightly populated ($n_\lambda = 0.1$),[7,24] and this could explain the difference in the total rotational strengths for the $^1A_{1g} \rightarrow {}^1T_{1g}$ absorption in the dmbn and pn complexes. An additional factor that could influence the CD of the dmbn complex relative to the pn complex is the slight increase in puckering of the dmbn chelate ring relative to the pn.[7] The much smaller size of the CD under the $^1A_{1g} \rightarrow {}^1T_{1g}$ band for the complex $[Co(NH_3)_4((S)\text{-pen})]^{3+}$ has been ascribed to a vicinal effect arising from the polarizable phenyl group.[4]

For the above three tetraammine complexes, if water is replaced by dimethyl sulfoxide as solvent, there is a slight increase in the size of the two Cotton effects under the $^1A_{1g} \rightarrow {}^1T_{1g}$ absorption. Evidence was obtained for $[Co(NH_3)_4(pen)]^{3+}$ to show that this change with solvent was consistent with an increase in the stereoselective solvation of the NH_2 protons, with NH_{eq} being more strongly solvated than NH_{ax}.[4]

(ii) $[Co(CN)_4((S)\text{-dmbn})]^-$. The lower energy $^1A_{1g} \rightarrow {}^1A_{2g}$ component of the $^1A_{1g} \rightarrow {}^1T_{1g}$ absorption has a small positive Cotton effect and the $^1A_{1g} \rightarrow {}^1E_g$ component a larger negative, as has been found for $[Co(CN)_4((S)\text{-pn})]^-$.[25] For the analogous phenyl compound, $[Co(CN)_4((S)\text{-pen})]^-$, only a negative is observed corresponding to the $^1A_{1g} \rightarrow {}^1E_g$ Cotton effect.[4] The total negative rotational strength under the $^1A_{1g} \rightarrow {}^1T_{1g}$ for the aqueous solutions varied in the order dmbn > pn >> pen, as was found for the tetraammine complexes.

Solvation of these complexes involves proton donation by the solvent at the nitrogen of the coordinated cyanide ligands, which causes an increase in Δ for the cyanide,[26,27] which in turn gives rise to a larger tetragonal splitting of the cubic absorption bands.[28] If the rotational strengths of the individual components did not vary, this would still lead to an increase in the observed Cotton effects as the degree of protonation increased because the increased separation of the transitions would lead to a lower degree of cancellation for the positive and negative Cotton effects. The ability of the solvents to donate protons increases in the order $(CH_3)_2SO << CH_3OH << H_2O$.[29] This is reflected in the increase in the energy of the $^1A_{1g} \rightarrow {}^1T_{1g}$ absorption: $(CH_3)_2SO$, 362; CH_3OH, 355; H_2O, 352 nm. The aqueous solution shows the largest Cotton effects consistent with the greater tetragonal splitting.

Solvation of the tetracyano(diamine)cobalt(III) complexes also involves electron donation by the solvent to the NH_2 protons. Due to the axial-equatorial relationship of the NH_2 protons, and the difference in the interactions of these protons with other atoms in the complex, they are solvated to different degrees, and this difference in the strength of the interaction between the solvent and the NH_2 protons varies with solvent and should give rise to a concomitant change in the size of the chemical shift difference between the two protons (ΔN, Table II). For $[Co(CN)_4((S)\text{-dmbn})]^-$ the $N(1)H_2$ group that is removed from the bulky *tert*-butyl group has a chemical shift difference, $\Delta N(1)$, which increases as the ability of the solvent to donate electrons[29] increases. However, this is not observed for $N(2)H_2$ where dimethyl sulfoxide, the strongest electron donor of the solvents studied, has a considerably smaller value of $\Delta N(2)$ than water or methanol. This reflects the larger molecular volume of dimethyl sulfoxide and its greater unfavorable interactions with the *tert*-butyl group.

The stereoselective solvation of the NH_2 group can markedly affect the CD of diamine complexes.[8] However, the total asymmetry introduced at the N donors as measured by $\sum \Delta N$ (Table II) does not vary significantly for $[Co(CN)_4((S)\text{-dmbn})]^-$ with water, methanol, and dimethyl sulfoxide, and therefore this factor should not contribute to the observed differences in the CD, although it will contribute to the actual CD spectra for the complex.

Under the $^1A_{1g} \rightarrow {}^1T_{2g}$ absorption, two Cotton effects are observed, a small positive and a very small negative. The

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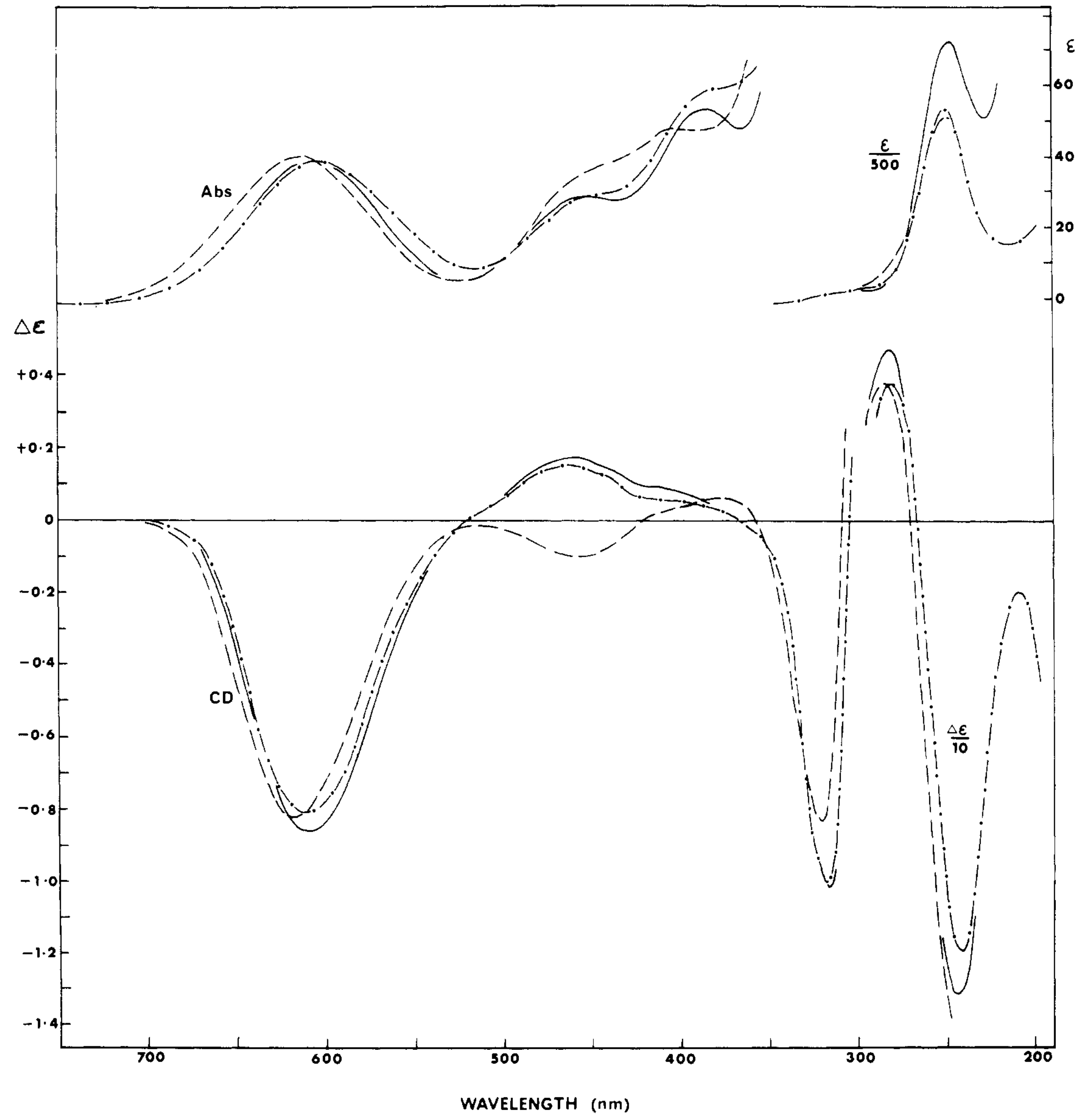

Figure 4. UV–visible absorption and circular dichroism spectra of *trans*-$[CoCl_2((S)\text{-dmbn})_2]^+$ in acetonitrile (—) as the tetraphenylborate salt and in methanol (–•–) and dimethyl sulfoxide (- - -) as the perchlorate salt.

charge-transfer region shows a large negative Cotton effect. These bands were also observed for $[Co(CN)_4((S)\text{-pn})]^-$.[26]

(iii) *trans*-$[CoCl_2((S)\text{-dmbn})_2]^+$. For the analogous 1,2-propanediamine[8] and 1-phenyl-1,2-ethanediamine[4] complexes, the solvent has been observed to alter greatly the CD spectra. In solvents such as acetonitrile that do not solvate the NH_2 groups strongly, and therefore do not introduce an additional source of dissymmetry by creating an asymmetric donor group, the $^1A_{1g} \rightarrow {}^1E_g$ Cotton effect is negative and the $^1A_{1g} \rightarrow {}^1A_{2g}$ positive. However, for strongly solvating solvents such as dimethyl sulfoxide, the $^1A_{1g} \rightarrow {}^1E_g$ Cotton effect is less negative and the $^1A_{1g} \rightarrow {}^1A_{2g}$ Cotton effect changes sign. The change in the Cotton effects, especially the $^1A_{1g} \rightarrow {}^1A_{2g}$ component has been found generally to mirror the $\sum\Delta N$ values.[4,8] These effects are again found for $[CoCl_2((S)\text{-dmbn})_2]^+$.

Acetonitrile has a low electron-donor power,[29] and its solvation of the NH_2 protons will not significantly contribute to the ΔN values. Thus for the pn[8] and dmbn complexes, $\Delta N(1)$ is 0. The $\Delta N(2)$ values show differences in the long-range anisotropic shielding of the axial and equatorial amine protons by the substituent: pn, 0.75; dmbn, 0.53. Because the solvent is able to interact more strongly with the equatorial protons than the axial protons, as the donor power of the solvent increases, the $\Delta N(1)$ and $\Delta N(2)$ values should also increase in size, notwithstanding any major long-range anisotropic shielding contribution to these values by the solvent. Methanol solvates more strongly than acetonitrile, but dimethyl sulfoxide donates electrons much more strongly than both.[29] The $\Delta N(1)$, $\Delta N(2)$, and $\sum\Delta N$ values increase in the order acetonitrile, methanol, and dimethyl sulfoxide for the dmbn and pn complexes. However, the bulk of the *tert*-butyl group restricts the solvation at $N(2)H_2$ for the dmbn complex compared to the pn complex, especially for the larger dimethyl sulfoxide, and the value of $\sum\Delta N$ for *trans*-$[CoCl_2((S)\text{-dmbn})_2]^+$ is significantly less than for the pn complex. This smaller degree of asymmetry introduced at the nitrogens via solvation results in a smaller change in the observed CD with solvent and noticeably in the smaller negative Cotton effect for the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition in dimethyl sulfoxide.

For *trans*-$[CoCl_2((S)\text{-pen})_2]^+$ the asymmetry introduced at the nitrogens via solvation as measured by the $\sum\Delta N$ values is much greater than for both the above complexes, and the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition has a large negative Cotton effect in dimethyl sulfoxide and even has a negative Cotton effect in methanol.

The charge-transfer region for *trans*-$[CoCl_2((S)\text{-dmbn})_2]^+$ has three Cotton effects. For the analogous *trans*-1,2-cyclohexanediamine (chn)[30] and pn[31] complexes, the corresponding

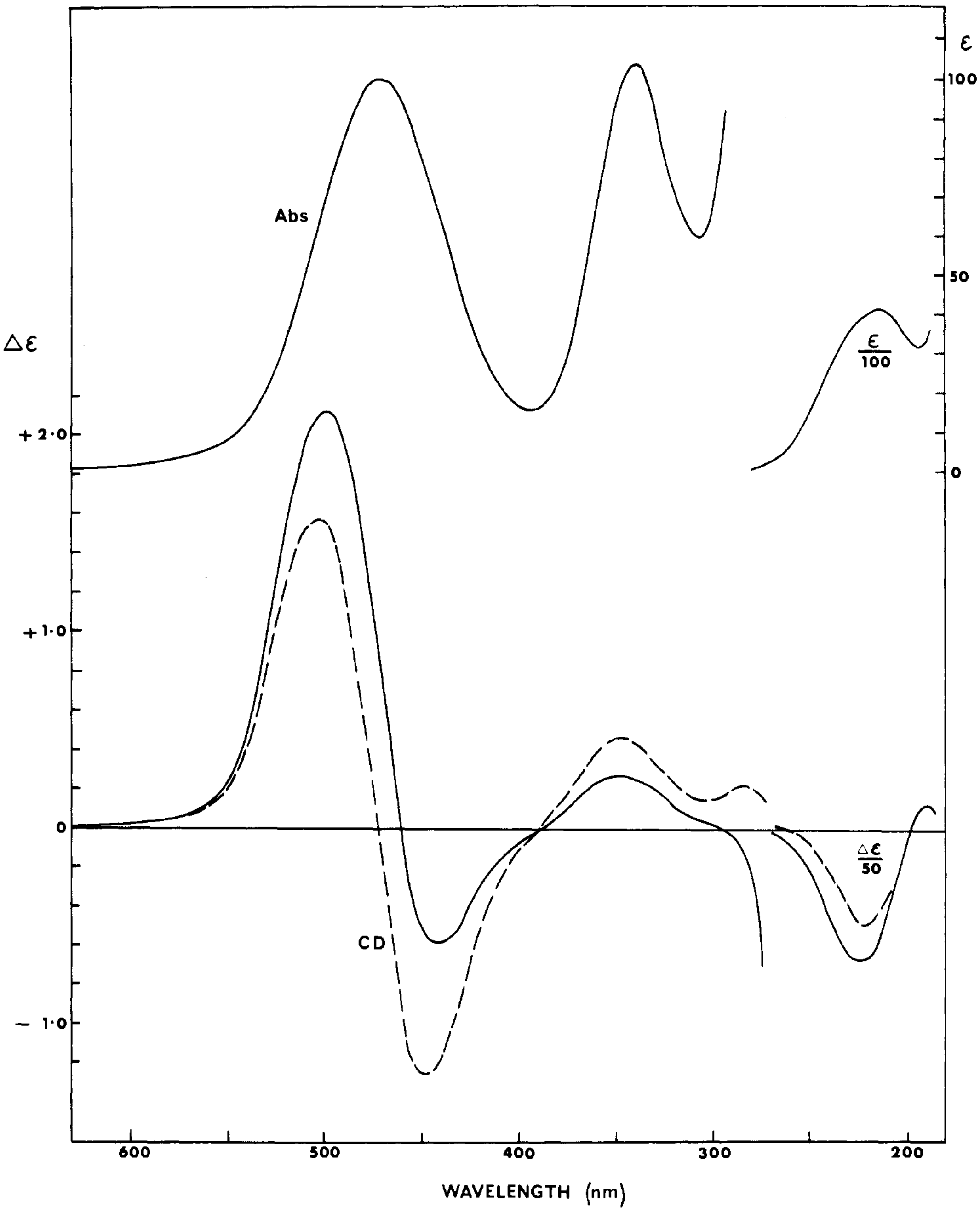

Figure 5. UV–visible absorption and circular dichroism spectra of Λ-[Co((*S*)-dmbn)$_3$]Cl$_3$ in water (—) and in 0.5 M Na$_3$PO$_4$ (---).

lower energy negative and positive bands have been assigned to $p_\pi \rightarrow d_{z^2}$ transitions and the higher energy negative to a $p_\sigma \rightarrow d_{z^2}$ transition.

trans-[CoCl$_2$((*S*)-dmbn)$_2$]$^+$ can exist in two geometrical isomeric forms with the two *tert*-butyl groups cis or trans. The ^{13}C spectrum shows no evidence that two isomers are present in the isolated compound.

(iv) [Co((*S*)-dmbn)$_3$]$^{3+}$. There are four possible isomers for this complex resulting from the facial and meridional geometric isomers, and the Λ and Δ distributions of chelates. The conformation is restricted to the δ chirality due to the necessity for the *tert*-butyl group to be equatorial. Statistically the meridional isomer should have three times the population of the facial isomer. If the complex had been prepared under equilibrium conditions, say over charcoal at elevated temperatures, both isomers would have been expected to be present, probably in their statistical ratio, as has been found for [Co(pn)$_3$]$^{3+}$.[11] In addition, both the Λ and Δ distributions of chelates would have been present; although based on the [Co(pn)$_3$]$^{3+}$ system,[11,32] the Δ(δδδ) configuration would have been present in only relatively small concentration.

Column chromatography with Sephadex cation exchanger SP-C25 and with 0.1 M sodium orthophosphate as eluent, that had successfully separated the four isomers for [Co(pn)$_3$]$^{3+}$,[11] gave only one band for [Co((*S*)-dmbn)$_3$]$^{3+}$ isolated by the above two methods of preparation. The ^{13}C NMR spectrum of the isolated complex has only one signal for each different type of carbon, and the ^{1}H NMR resonance for C(CH$_3$)$_3$ shows only one sharp signal, unbroadened by ^{59}Co coupling. For the meridional isomer, each carbon and the C(CH$_3$)$_3$ protons should yield three resonances as the three chelates are not related by symmetry. This has been observed for related complexes such as [Co(ibn)$_3$]$^{3+}$, where ibn is 2-methyl-1,2-propanediamine,[9] but three resonances for each carbon were

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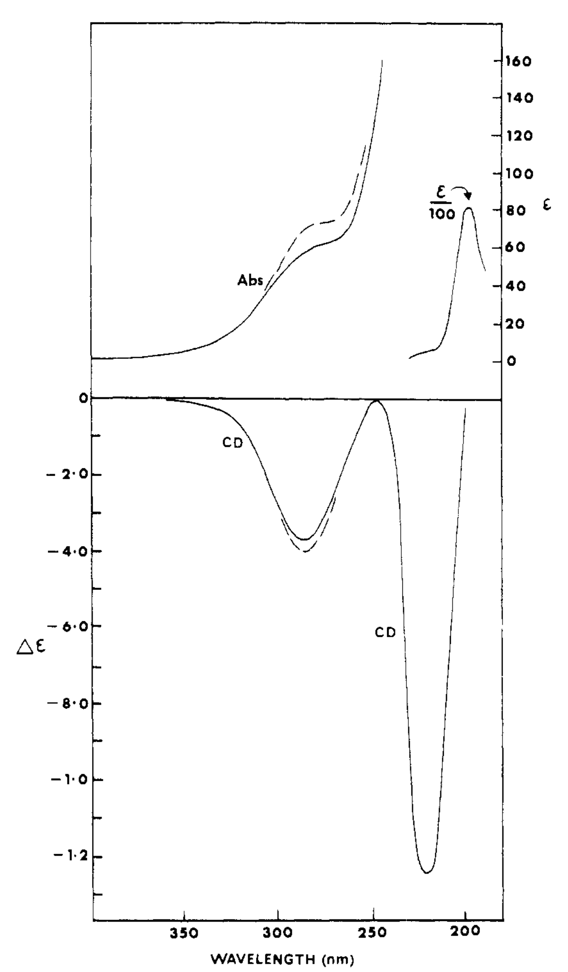

Figure 6. UV–visible absorption and circular dichroism spectra of $[Pt(NH_3)_2((S)\text{-dmbn})]Cl_2$ in water (—) and dimethyl sulfoxide (---).

not observed at 22.63 MHz for *mer*-Λ(λλλ)-$[Co((R)\text{-pn})_3]^{3+}$,[33] and for Δ(λλλ)-$[Co((R)\text{-pn})_3]^{3+}$ the ^1H NMR spectrum at 251 MHz showed only two doublets for the CH_3 groups in the ratio 2:3.[34] The evidence is consistent with the facial isomer, but the data are not conclusive. However, as $^{13}CH_3$ and $^{13}CH_2$ do have different chemical shifts for *mer*-Λ- and *fac*-Λ-$[Co((R)\text{-pn})_3]^{3+}$,[33] the ^{13}C spectrum supports the above conclusion from the chromatography that only one isomer is present. The Δ and Λ configurations for related complexes do show different ^{13}C resonances for the two configurations. For example, Λ-$[Co((R,R)\text{-bn})_3]^{3+}$, where bn is 2,3-butanediamine, has a ^{13}CH resonance at δ 57.4 and the Δ isomer has the same resonance at δ 58.6.[35] For the Λ and Δ isomers of $[Co((R)\text{-pn})_3]^{3+}$, the CH resonances are at δ 53.7 and 55.0, respectively.[33] The fact that only one resonance is observed for CH in $[Co((S)\text{-dmbn})_3]^{3+}$ shows the isolated complex has predominantly one configuration which, as stated above, would be Λ. For $[Co((R)\text{-pn})_3]^{3+}$ the four stereoisomers, *mer*-Δ, *fac*-Δ, *mer*-Λ, and *fac*-Λ, give separate ^{59}Co resonances.[36-38] The samples of $[Co((S)\text{-dmbn})_3]^{3+}$ isolated here give a single relatively sharp ^{59}Co resonance which confirms the above conclusion that only one stereoisomer is present. In conclusion, under the nonequilibrium experimental conditions used here to prepare $[Co((S)\text{-dmbn})]^{3+}$, only one stereoisomer was isolated. It has the Λ(δδδ) configuration, and the experimental evidence is consistent with the facial isomer.

The CD spectra of tris(diamine)cobalt(III) complexes have major contributions from the configurational effect and the conformational effect. The Λ(δδδ) isomers of $[Co((S)\text{-dmbn})_3]^{3+}$ and $[Co((S)\text{-pn})_3]^{3+}$ have very similar CD spectra in the d–d and in the charge-transfer regions.[11,12,39,40] The analogous complex with 1-phenyl-1,2-ethanediamine[14] again shows some differences to the alkyl diamines in the d–d region with a larger positive Cotton effect for the $^1A \rightarrow {}^1E$ component and a slightly smaller negative for the $^1A_1 \rightarrow {}^1A_2$ component. This could again be due to a vicinal effect from the polarizable phenyl group. In the literature, there are reports that the $\Delta\epsilon_{max}$ value for the charge transfer can be factorized into contributions from the configurational effect and conformational effect.[11,12] Values of −30[11] and −20[12] have been obtained for the Λ configuration and −3,[11] and −8[12] for each δ conformation. Neither set of values agrees with the value of −34 found for Λ-$[Co((S)\text{-dmbn})_3]^{3+}$.

The effect of added phosphate ion on the observed CD of Λ-$[Co((S)\text{-dmbn})_3]^{3+}$ is similar to that observed for analogous diamine complexes:[41,42] the $^1A_1 \rightarrow {}^1E$ component is reduced and the $^1A_1 \rightarrow {}^1A_2$ component is increased in size. This has been attributed to the stereoselective ion pairing of the phosphate along the C_3 axis to the equatorial NH protons parallel to the C_3 axis rendering the nitrogens asymmetric with the same configuration.[43]

Platinum(II) Complexes. $[Pt(NH_3)_2((S)\text{-dmbn})]^{2+}$. The absorption and CD spectra of diammine((*S*)-diamine)platinum(II) complexes show two d–d peaks at about 280 and 220 nm and a charge-transfer peak at 200 nm. All three Cotton effects are negative for the *S* configuration.[44-46] For $[Pt(NH_3)_2((S)\text{-pn})]^{2+}$ the low-energy band has been assigned to the spin-forbidden $^1A_1 \rightarrow {}^3E_g$ (D_{4h}) transition, which gains intensity through spin–orbit coupling, and the Cotton effect at 220 nm has been assigned to the $^1A_{1g} \rightarrow {}^1E_g$ transition.[44]

As the CD of the (*S*)-pn complex is approximately half the size of the (*S,S*)-*trans*-1,2-cyclohexanediamine complex[44] that is restricted to the δ conformation, it has previously been concluded that the δ conformation is 75% populated in $[Pt(NH_3)_2((S)\text{-pn})]^{2+}$.[1] Recent conformational analyses based on vicinal proton coupling constants[7,24] and vicinal ^{195}Pt–^{13}C coupling constants[24,47] have concluded that in the pn complex the δ conformation is 66% and 72% populated, respectively. If the size of the spin-allowed transition, $^1A_{1g} \rightarrow {}^1E_g$, for $[Pt(NH_3)_2((S)\text{-dmbn})]^{2+}$ is taken as a measure of the conformational effect for a δ conformation (Δε −1.25), the observed value[44] of Δε −0.51 for $[Pt(NH_3)_2((S)\text{-pn})]^{2+}$ would correspond to the δ conformation having a 70% population, in excellent agreement with the NMR conformational analyses.

The CD and absorption spectra of $[Pt(NH_3)_2((S)\text{-dmbn})]^{2+}$ both show a slight increase in intensity of the low-energy band on changing the solvent from water to dimethyl sulfoxide. Because of the absence of apical ligands in the square-planar platinum(II) complexes, the differences in the strength of solvation at the equatorial and axial NH_2 protons would not be as marked as in the octahedral complexes, and hence the degree of asymmetry introduced at the nitrogens and the

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changes in CD with solvent are less significant.

In $[Pt(NH_3)_2((S)\text{-dmbn})]^{2+}$ the quaternary carbon has an approximate trans relationship with the Pt. The vicinal coupling between the carbon and ^{195}Pt is therefore maximized, giving a value of 41 Hz. An axial carbon has a torsional angle with Pt of about 90° and therefore has a very small coupling with ^{195}Pt. In $[Pt(NH_3)_2(meso\text{-bn})]^{2+}$ and $[Pt(NH_3)_2(ibn)]^{2+}$, the δ and λ conformations are equally populated, and hence the observed $^3J_{PtC}$ values, 27.3 and 22.4 Hz, respectively, are the averages of the values for the axial and equatorial methyls.[48] The methyl groups in $[Pt(NH_3)_2((R,R)\text{-bn})]^{2+}$ are predominantly, but not exclusively, in equatorial orientations, and have a value of 49.8 Hz for $^3J_{PtC}$.[48] A direct comparison of the $^3J_{PtC}$ values for the equatorial quaternary carbon in the dmbn complex and the equatorial methyl carbons in the above complexes is not possible because of the different substituent effects.

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Registry No. $[Co(NH_3)_4((S)\text{-dmbn})](NO_3)_{1.5}(ClO_4)_{1.5}$, 80145-88-6; *trans*-$[CoCl_2((S)\text{-dmbn})_2]ClO_4$, 80145-90-0; *trans*-$[CoCl_2((S)\text{-dmbn})_2]BPh_4$, 80145-91-1; Λ-$[Co((S)\text{-dmbn})_3]Cl_3$, 80225-17-8; Λ-$[Co((S)\text{-dmbn})_3](ClO_4)_{1.5}Cl_{1.5}$, 80225-15-6; $[Pt(NH_3)_2((S)\text{-dmbn})]Cl_2$, 80145-76-2; $K[Co(CN)_4((S)\text{-dmbn})]$, 58410-52-9; *trans*-dichlorotetrakis(pyridine)cobalt(III) chloride, 27883-34-7.

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Gas-Phase Helium I Photoelectron Spectra of Methinyltricobalt Enneacarbonyl Clusters

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The electronic structure of $Co_3(CO)_9CY$ clusters, where Y = H, F, Cl, Br, I, CH_3, CF_3, or $COOCH_3$, is discussed on the basis of their He I excited gas-phase photoelectron spectra. A qualitative energy level diagram has been afforded which allows a satisfactory discussion of the PE data. The most interesting feature of our interpretative model is the presence of a molecular orbital of e symmetry which accounts for a large portion of the interaction between the Co_3 triangle and the apical carbon atom C_{ap} and for the electron transmission from the apical substituent Y and the cobalt atoms via a resonance-type mechanism. In agreement with previous NQR and IR data, evidence for significant $Y \rightarrow C_{ap}$ π-bonding donation with Y = Cl, Br, or I is presented. The relationships existing between the present clusters and molecules of type $M_3(CO)_{12}$ and $(\mu\text{-}CH_2)[ML_n]_2$ have been stressed.

Introduction

Since it was suggested that transition-metal clusters can offer good models to mimic substrate–surface interaction,[2] a large number of spectroscopic studies have been devoted to this class of molecules.

Until now, however, few gas-phase photoelectron (PE) investigations have been carried out,[3] although these compounds often show good stability and volatility which make them suitable for PE investigations.

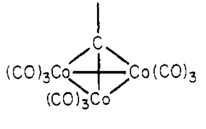
In order to get more information about the potentiality of this technique as applied to transition metal clusters and as a further development of our previous studies,[3a,4,5] we have undertaken a PE study of the series $Co_3(CO)_9CY$ (Y = H, F, Cl, Br, I, CH_3, CF_3, $COOCH_3$),[6] whose chemical and structural features have received widespread attention in the past 20 years.[7]

Table I. Ionization Energies (eV) of the $Co_3(CO)_9CY$ Clusters[a]

	band label					
cluster	A′ (S′)	A″	B′	B″	C′ (S″)	C″
H	8.75 (7.9)	10.23			14.0	18.0
CH_3	8.58 (7.9)	9.93			14.2 (12.7)	17.7
CF_3	8.96 (8.2)	10.40			14.3 (16.2)	17.9
$COOCH_3$	8.73 (8.1)	9.80	11.57		14.2	17.9
F	8.96 (8.2)	10.24			14.3	18.1
Cl	8.63 (7.9)	9.85	12.28		14.1	17.7
Br	8.73 (8.0)	9.80	11.55		14.2 (12.8)	17.9
I	8.76 (8.1)	9.77	10.94	12.46	14.1	17.8

[a] Values in parentheses refer to shoulders.

A trigonal-pyramidal structural core Co_3C (C_{3v} symmetry) was early inferred from chemical evidence[8] and IR measurements[9] and subsequently confirmed by several structural determinations.[7]



The peculiar arrangement of three Co atoms with the apical

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