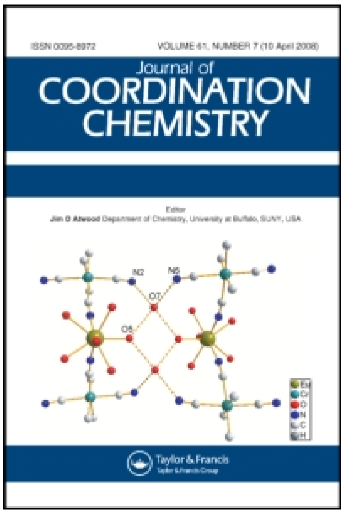

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CIRCULAR DICHROISM OF BIS(DIMETHYLGLYOXIMATO)COBALT(III) COMPLEXES CONTAINING OPTICALLY ACTIVE AMINES

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The preparations and circular dichroism (CD) spectra of a series of bis(dimethylglyoximato)cobalt(III) complexes, each containing two asymmetric unidentate amines in trans positions, are reported. Tentative spectral assignments are made for the *d–d* region on the basis of effective D_{4h} molecular symmetry. In all cases the rotational strengths observed for the aromatic amine complexes are larger than those observed for the alkyl amine complexes.

INTRODUCTION

There are few studies of the vicinal effect of optically active amines in cobalt(III) complexes. Recently several studies have been reported[1–3] for complexes of the type $[(\mathrm{Co(NH_3)_5amine}]^{n+}$ with effectively octahedral symmetry. In these complexes the contribution of the optically active amines to the rotary strength is not complicated by the presence of other contributions which are often larger than the vicinal effects involved. We were interested in extending this type of study to complexes of a rigid geometrical structure and lower molecular symmetry, yet keeping contributions aside from the vicinal effect at a minimum. For this purpose we report here a series of complexes containing optically active α-substituted ethylamines of the general formula *trans*-$[\mathrm{Co(amine)_2(Hdmg)_2}]^+$ where Hdmg is the dimethylglyoximate ion. It has been shown that such complexes have the trans geometry[4] for the two unidentate ligand and the $\mathrm{Co(Hdmg)_2}$ moiety is expected to be essentially planar. Contributions of the vicinal effect of the axial asymmetric amines may then be examined with little change of the planar $\mathrm{Co(Hdmg)_2}$ expected. Similar dimethylglyoxime complexes of cobalt are of interest as models of vitamin B_{12}.

EXPERIMENTAL SECTION

Materials

Most of the optically active amines were purchased in their resolved form:
S-(–)-1-phenylethylamine,
S-(+)-1-methyl-2-phenylethylamine and
S-(–)-1-(1′-naphthyl)-ethylamine
from the Aldrich Chemical Corp. *S*-(+)-1-methylpropylamine from Norse Laboratories Inc. *R*-(–)-1,3-dimethylbutylamine ($[\alpha]^{25}_{D} = -11.3°$ (neat); lit.[5,6] $-10.7°$ (neat); $-11.2°$ (neat)) and *R*-(–)-1-methylhexylamine ($[\alpha]^{25}_{D} = -6.7°$ (neat); lit.[6] $-6.7°$ (neat)) were prepared by the method of Mazur[6] via their tartrate salts. The absolute configurations of all of these amines have been established previously.[6–10]

The amine complexes were prepared from *trans*-dichlorobis(dimethylglyoximato)cobaltic acid, obtained by the method of Babko[11] and formulated $\mathrm{H[CoCl_2(Hdmg)_2]}$ or $\mathrm{CoCl_2(Hdmg)(H_2dmg)}$).[12]

Preparation of the Trans-bis(amine)bis(dimethylglyoximato)cobalt(III) Chloride Complexes, trans-$[\mathrm{Co(amine)_2(Hdmg)_2]Cl \cdot H_2O}$

All of the amine complexes were prepared by combining the resolved amine (20 mmol) dissolved in 3 ml of absolute ethanol with $\mathrm{H[CoCl_2(Hdmg)_2]}$ (1.8g, 5 mmol) suspended in 3 ml of water. The mixture was stirred to insure complete mixing and heated until all solids dissolved. The dark brown solution was allowed to cool to room temperature and the crystalline product which precipitated was filtered, washed with acetone and then recrystallized from a minimum of hot water-ethanol (1:1). The complexes prepared using the alkyl amines were bright orange in color and the complexes prepared from the aromatic amines were brown-orange. Overall yields for the recrystallized products ranged from 20–60%. Analyses are given in Table I. All of the

Table I.
Analyses of Trans-[Co(amine)$_2$(Hdmg)$_2$] Cl Complexes

Amine	Formula	Calcd. (%)		
		C	H	N
S-(-)-1-(1'-naphthyl)ethylamine $C_{10}H_7CH(CH_3)NH_2$	$CoC_{32}H_{40}N_6O_4Cl \cdot H_2O$	56.10	6.17	12.26
S-(+)-1-methyl-2-phenylethylamine $C_6H_5CH_2CH(CH_3)NH_2$	$CoC_{26}H_{40}N_6O_4Cl \cdot H_2O$	50.94	6.90	13.70
S-(-)-1-phenylethylamine $C_6H_5CH(CH_3)NH_2$	$CoC_{24}H_{36}N_6O_4Cl \cdot H_2O$	49.27	6.54	14.36
S-(+)-1-methylpropylamine $C_2H_5CH(CH_3)NH_2$	$CoC_{16}H_{36}N_6O_4Cl$	40.81	7.70	17.84
R-(+)-1-methylhexylamine $CH_3(CH_2)_4CH(CH_3)NH_2$	$CoC_{22}H_{48}N_6O_4Cl$	47.60	8.71	15.14
R-(-)-1,3-dimethylbutylamine $CH_3CH(CH_3)CH_2CH(CH_3)NH_2$	$CoC_{20}H_{44}N_6O_4Cl$	45.58	8.41	15.94

complexes were soluble in ethanol and dimethyl sulfoxide. The alkyl amine complexes were soluble in water, but the aromatic amine complexes were only slightly soluble.

Spectra

The absorption spectra were recorded on a Cary 14 spectrophotometer at room temperature using tungsten and hydrogen sources. The CD spectra were recorded on a Cary Model 61 spectropolarimeter using a xenon source. Both spectra were obtained using 1 cm quartz cells with absolute ethanol as solvent. Identical spectra were also obtained in water and dimethyl sulfoxide.

Analyses

Elemental analyses were performed by Chemalytics, Inc., Tempe, Arizona.

RESULTS AND DISCUSSIONS

Analyses for the complexes of the general type [Co(amine)$_2$(Hdmg$_2$)]Cl are reported in Table I. Ablov[13] has shown that this formulation represents the principal product in the reaction of H[CoCl$_2$(Hdmg)$_2$] with an excess of aromatic amine. Amines with the *S*-absolute configuration were used wherever available. The complexes are considered to have trans geometry with the optically active α-substituted ethylamines occupying trans axial positions relative to the planar Co(Hdmg)$_2$ moiety.

The electronic spectra, for the amine complexes considered here (Figures 1 and 2), are consistent with those reported by Ablov, Zsako, and coworkers[13-15] for *trans*-[Co(amine)$_2$(Hdmg)$_2$]$^+$ where the amine is ammonia, analine or one of several substituted aromatic amines. In general, the electronic absorption spectra are relatively featureless for

Table I *(continued)*

	Found (%)			
Cl	C	H	N	Cl
5.17	56.24	6.39	12.30	5.17
	51.09	6.82	14.04	
	48.93	6.41	14.41	
7.52	40.75	7.74	17.76	7.51
	47.88	8.85	15.28	
	45.81	8.39	16.01	

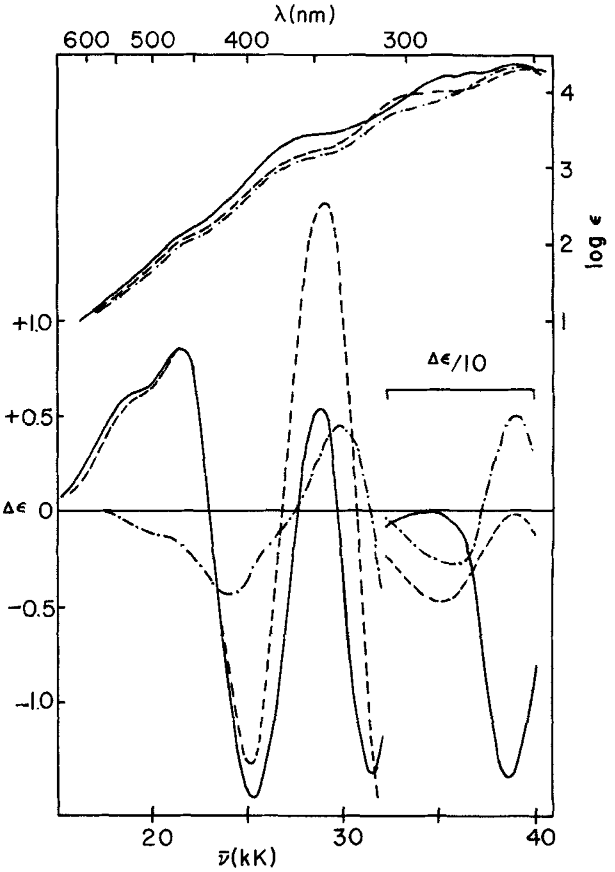

FIGURE 1 Circular dichroism and absorption spectra of *trans*-[Co(Hdmg)$_2$(*S*-(−)1-(1′-naphthyl)ethylamine)$_2$]$^+$ (————), *trans*-[Co(Hdmg)$_2$(*S*-(−)-1-phenylethylamine)$_2$]$^+$ (– – –), and *trans*-[Co(Hdmg)$_2$(*S*-(+)-1-methyl-2-phenylethylamine)$_2$]$^+$ (–.–.).

dimethylglyoxime complexes, making a detailed curve analysis unwarranted. There is great overlap of intense bands from the ultraviolet through the visible regions. From the high intensities it seems likely that allowed transitions mix with the *d–d* transitions. Because of the poorly defined peaks, assignments can only be tentative. Since the Co(III) ion is coordinated to 6 nitrogens, splitting resulting from the deviation from O_h symmetry might be expected to be obscured. For the aromatic amine complexes (Figure 1), the lowest energy peak (*ca.* 21 kK) is in a reasonable position for the $T_{1g}(O_h)$ band. Its intensity is high for a *d–d* band, indicating mixing or overlap with allowed bands. The low energy side of this band is drawn out more than expected for a Gaussian band, suggesting the presence of a shoulder which might be attributed to tetragonal distortion of the O_h field. The next peak (*ca.* 28 kK) corresponds to a band assigned as a charge transfer transition, Co^{3+} to the Hdmg ligand, by Matsumoto *et al.*[16] This is the region in which the $T_{2g}(O_h)$ band is expected, but presumably it is masked by the more intense band.

For the alkyl amine complexes (Figure 2), there are two maxima in the low energy $T_{1g}(O_h)$ region centered at *ca.* 19 and 22–23 kK. These are likely to be the tetragonal components, revealing the deviation from O_h symmetry. The next peak (*ca.* 27 kK) is probably the same charge transfer transition mentioned above, which masks the T_{2g} band.

All complexes (Figures 1 and 2) show additional peaks at 39 and *ca.* 32 kK. These have been assigned by Zsako *et al.*[15] to the coordinated dimethylglyoximate ligands. Dimethylglyoxime has, in the free state,[17] a strong band at 37.7 and a weaker one at 31.5–32.0 kK.

Circular dichroism

In this first report of the circular dichroism of such complexes, it is interesting to note the clarity and wealth of information present in comparison to the rather featureless absorption curves. Even though the CD peaks are well defined, significant overlap must exist, again precluding detailed curve analysis.

In the CD spectra for all of the amine complexes (Figures 1 and 2), except for *trans*-[Co(Hdmg)$_2$(*S*-(+)-1-methyl-2-phenylethylamine)$_2$]$^+$, there are at least two low energy transitions, in the $^1T_{1g}(O_h)$ region, consistent with D_{4h} molecular symmetry. These components, ^1E_g and $^1A_{2g}$, are identified with the lowest energy CD peak which shows a pronounced shoulder (Figures 1 and 2). It is interesting that the shoulder appears at higher energy for the alkylamines (Figure 2), but it is even more pronounced and at lower energy for the aromatic amines, (Figure 1). Two peaks of the same sign represent the minimum number of components needed to account for the CD curves in the region of the lowest energy absorption band. Three peaks of alternating sign could also account for the observed curves, but there is insufficient basis for this interpretation. Only one negative CD peak (*ca.* 20 kK) appears in this region for the *S*-(+)-1-methyl-2-phenylethylamine complex (Figure 1). The position, the drawn out shape, and the sign of this band relative to those of the other complexes, suggest that the two components have opposite signs in this case and largely cancel because of small tetragonal splitting.

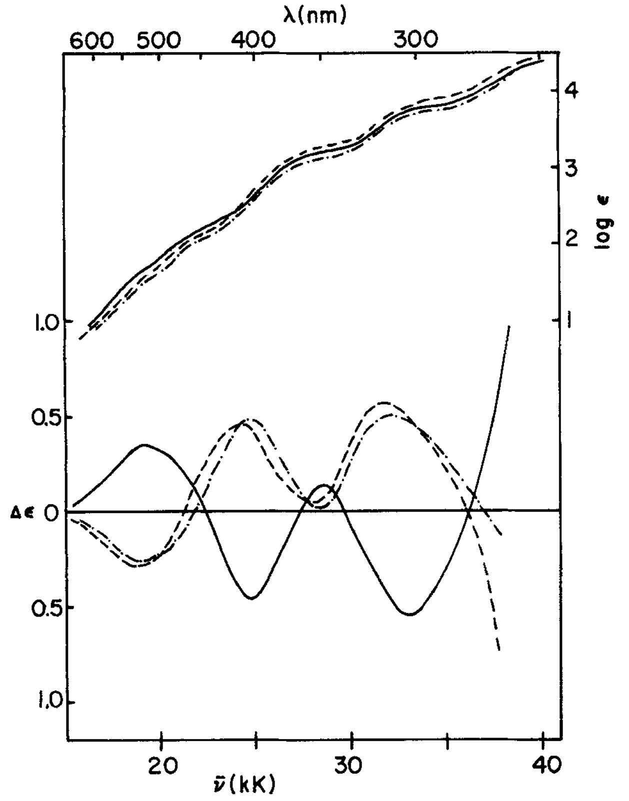

FIGURE 2 Circular dichroism and absorption spectra of *trans*-[Co(Hdmg)$_2$(*S*-(+)-1-methylpropylamine)$_2$]$^+$ (————), *trans*-[Co(Hdmg)$_2$(*R*-(−)-1,3-dimethylbutylamine)$_2$]$^+$ (– – –), and *trans*-[Co(Hdmg)$_2$(*R*-(−)-1-methylhexylamine)$_2$]$^+$ (–.–.).

The CD peaks at *ca.* 24–26 kK for all complexes are probably associated with the $T_{2g}(O_h)$ transition which is masked in the absorption spectra. For most complexes, the CD intensities are weaker in the T_{2g} region than in the T_{1g} region. The high intensities of the CD peaks in this region for the complexes reported here indicate mixing with allowed charge transfer or ligand transitions.

In the region 28.6–30 kK, the CD peaks vary in magnitude depending on the amine used, being largest positive for *S*-(−)-1-phenylethylamine and nearly zero for *R*-(−)-1-methylhexylamine and *R*-(−)-1,3-dimethylbutylamine. These are likely to be associated with charge transfer between the asymmetric axial amine and the cobalt(III) ion. Free ligand transitions of the aromatic amines are at much higher energies and relate to the CD peaks observed between 32 and 40 kK for the various complexes. Free ligand electronic absorption and CD spectra obtained showed several overlapping maxima in the region 33–40 kK for the aromatic amines. No electronic absorption or CD spectra were observed for the free alkyl amines below 43 kK. The circular dichroism spectra for the alkyl amine complexes in the region 31–35 kK are then representative of free ligand and charge transfer dimethylglyoxime transitions, while the aromatic amine complexes contain, in addition, amine transitions. Due to the broad, overlapping bands it would be purely speculative to try to make specific assignments.

In all cases the rotational strengths observed for the aromatic amine complexes are larger than those observed for the alkyl amine complexes. This might be expected since the aromatic amine transitions occur at lower energies so that they might mix with the metal and charge transfer transitions to a greater extent. The complex curves permit only tentative assignments. The CD curves show promise for the study of closely related models of vitamin B_{12}.

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