tances differing by 0.05 Å. No attempt at fine-tuning this distance was attempted. The resulting bond lengths are reasonable, but there is a paucity of accurate bond length information on these systems to compare. It may be that all of these "predicted" bond lengths are too long.

Nevertheless, the results we have obtained using this model for the complexes of this study, and the results we have obtained on transition-metal halide and ethylenediamine complexes not reported here, are of very good accuracy. We feel these results are of sufficient accuracy to give the model disclosed here important utility for explaining and predicting the d–d spectra of transition-metal complexes in an efficient and inexpensive manner.[32]

As the bands of interest in this study are primarily d–d*, a configuration interaction including all single excitations generated from the SCF reference state plus all possible excitations within the d-orbital manifold as described seems most appropriate. A more economical CI limited to only single excitations reliably reproduces only the lower energy bands of these complexes, and the relative positions of the spin manifolds to each other are somewhat poorer. Single excited configuration interaction is required as the lowest level of acceptable theory in order to sort out properly the degeneracies of systems with high symmetry. For these particular complexes there is also a substantial mixing of configurations with different electron assignments, and this proves

particularly important in the d^8 complexes, where there is t^5e^3–t^4e^4 mixing as noted for $Ni(H_2O)_6^{2+}$. A CI limited to only single excitations would be of great utility in examining larger systems, and especially systems in which charge-transfer and ligand spectra are of prime interest, for most of the computing time is spent in the configuration interaction calculation. Such a treatment will be of utility only if the ground spin state of the central transition-metal ion is known in advance or if the single excitations alone are able to reliably yield the lowest energy metal ion configuration. Unfortunately, the latter is not always the case,[13–15,17] and we cannot recommend this procedure as a blind procedure, even within this model Hamiltonian.

The procedure that we do describe here, though, seems dependable, and we have been able to successfully calculate the spectroscopy of larger complexes such as the porphyrins, where d–d*, charge transfer, and ligand–(ligand)* transitions are all of interest.

Contribution from the Department of Chemistry, Faculty of Science,
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Circular Dichroism of Chromium(III) Complexes. 11. Chiroptical Evidence for Solution Structure of a Sexidentate Chelate Coordination Mode in Chromium(III) Complexes with edta and Related Ligands

Sumio Kaizaki* and Hitomi Mizu-uchi

The chiroptical spectra, specifically, circular dichroism, of the chiral edta (ethylenediaminetetraacetato)-like complexes of (*S*)-1,2-propylenediaminetetraacetate ((*S*)-pdta) and (*1S,2S*)-1,2-*trans*-cyclohexanediaminetetraacetate ((*S,S*)-cydta) with chromium(III) and magnetic circular dichroism of the corresponding racemates were measured in solutions of various acid concentrations and/or solid states as compared with those of the edtra (ethylenediaminetriacetato)-like complexes. It has been found that the chiroptical spectral variation in acid solution reflects a significant change of coordination mode in solution structures: a change from sexi- to quinquedentate edta coordination. This chiroptical behavior has substantiated the controversial solution structure of sexidentate edta coordination in the complexes more decisively than the recent ^2H NMR studies.

Introduction

Recently, there have been some significant developments in studies of the controversial sexi- or quinquedentate coordination of edta in [Cr(edta)]⁻[1–5] (where edta refers to ethylenediaminetetraacetate): the X-ray crystal structure analyses for the hydrogen and sodium forms[6,7] and the ^2H NMR studies for deuterated edta

and the closely related amino polycarboxylato complexes in solution.[8] Though these studies suggested possibilities of sexidentate edta coordination in solution, there has still remained some doubt of a pentagonal-bipyramidal structure with a sexidentate edta or a rapid exchange of the ligating atom (H_2O and acetate of the edta).[5b,8] There has been no direct spectroscopic information to prove the sexidentate octahedral coordination in solution so far.

Chiroptical spectroscopy in solution and/or the solid state will afford another kind of evidence for a sexi- or quinquedentate edta in a chromium(III) complex, since such spectra are expected to be more sensitive to the edta chelate coordination mode or to the change of the ligating atoms than are the ^2H NMR spectra.

This paper deals with the solution structure of edta-like complexes in comparison with solution and solid chiroptical spectra and in terms of spectral changes with acid concentration. As the chiroptical spectra, circular dichroism (CD) and magnetic circular dichroism (MCD) are utilized for chiral edta analogues such as

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Table I. Elemental Analysis Data of the Complexes

	C/%		H/%		N/%	
complex	found	calcd	found	calcd	found	calcd
Na[Cr{(S)-pdta}]·3H₂O	30.44	30.64	4.72	4.67	6.50	6.50
Na[Cr{(S,S)-cydta}]·4H₂O	34.34	34.36	5.30	5.36	5.60	5.72
[Cr{(S)-pdtra}(H₂O)]·1.75H₂O	32.19	31.17	5.36	5.38	7.91	8.08
[Cr{(S,S)-cydtra}(H₂O)]·2.5H₂O	35.97	36.00	5.84	6.04	6.92	7.00
[Cr{H(S)-pdta}(H₂O)]·2H₂O	31.60	32.28	5.05	5.17	6.71	6.84
[Cr{H(S,S)-cydta}(H₂O)]·2H₂O	37.12	37.34	5.39	5.82	6.08	6.22

Table II. Absorption Data of the edta-like Chromium(III) Complexes[a]

K[Cr(edta)] (44.7 mM,
in 10 mM HClO₄ at pH 5.5)
18.45 (208.9)   25.51 (119.6)

[Cr{(S)-pdta}]⁻ (ca. 5 mM)

H₂O (pH 5.0)	1 mM HClO₄ (pH 4.5)	1 M HClO₄ (pH 1.5)
18.45 (203.6)	18.44 (213.0)	18.38 (149.6)
25.56 (111.9)	25.63 (114.9)	26.04 (111.9)

[Cr{(S,S)-cydta}]⁻

H₂O (pH 5.0)	4 M HClO₄
18.45 (208.9)	18.38 (167.9)
25.44 (101.4)	25.97 (102.2)

[Cr(edtra)(H₂O)] 1 mM HClO₄	[Cr{(S)-pdtra}(H₂O)] 1 mM HClO₄	[Cr{(S,S)-cydtra}(H₂O)] 1 mM HClO₄
18.50 (133)	18.62 (134.9)	18.73 (140.2)
25.90 (107.0)	25.71 (101.0)	25.77 (99.3)

[a] In units of 10³ cm⁻¹ for the absorption maxima and mol⁻¹ dm³ cm⁻¹ for ε, the molar absorbance, in parentheses.

(S)-propylenediaminetriacetate and -tetraacetate ((S)-pdtra and (S)-pdta) and (1S,2S)-1,2-trans-cyclohexanediaminetriacetate and -tetraacetate ((S,S)-cydtra and (S,S)-cydta) complexes and the corresponding racemates, respectively. The solution and solid CD and/or MCD behavior will be examined with the aim of resolving the ambiguities that the recent ²H NMR studies have left for the sexidentate chelate coordination mode of the complexes in solution.

Experimental Section

Preparation of the Complexes. The following complexes were prepared by literature methods:

(1) [Cr(Hedta)(H₂O)],[9] K[Cr(edta)]·2H₂O,[7] [Cr(edtra)(H₂O)]·2H₂O,[4] [Cr(hedtra)(H₂O)]·H₂O,[4] and Na[Cr(rac-cydta)]·4.5H₂O.[10,11] hedtra refers to N-(2-hydroxyethyl)ethylenediaminetriacetate.

(2) Na[Cr{(S)-pdta}]·3H₂O, [Cr{H(S)-pdta}(H₂O)]·2H₂O, and [Cr{(S)-pdtra}(H₂O)]·1.75H₂O. The ligand, (S)-propylenediaminetriacetic acid, was prepared by the method of Blackmer et al.[12] with use of (S)-propylenediamine instead of ethylenediamine. The reaction mixture was used for the preparation of the complex without isolating the ligand. The (S)-pdtra complex together with Na[Cr{(S)-pdta}]·3H₂O was obtained in a manner similar to that for [Cr(edtra)(H₂O)] with successive use of a Dowex 1-X8 anion-exchange resin in the acetate form and a Dowex 50W-X8 cation exchanger in the hydrogen form. The sodium (S)-pdta complex was converted to the hydrogen form, [Cr{H(S)-pdta}(H₂O)]·2H₂O, by using a 50W-X8 cation-exchange resin in the hydrogen form.

(3) Na[Cr{(S,S)-cydta}]·4H₂O, [Cr{H(S,S)-cydta}(H₂O)]·2H₂O, and [Cr{(S,S)-cydtra}(H₂O)]·2.5H₂O. These complexes were prepared by methods similar to those used for the (S)-pdta and (S)-pdtra complexes with use of (1S,2S)-1,2-trans-cyclohexanediamine. The chiral diamines used were obtained by methods described elsewhere.[13]

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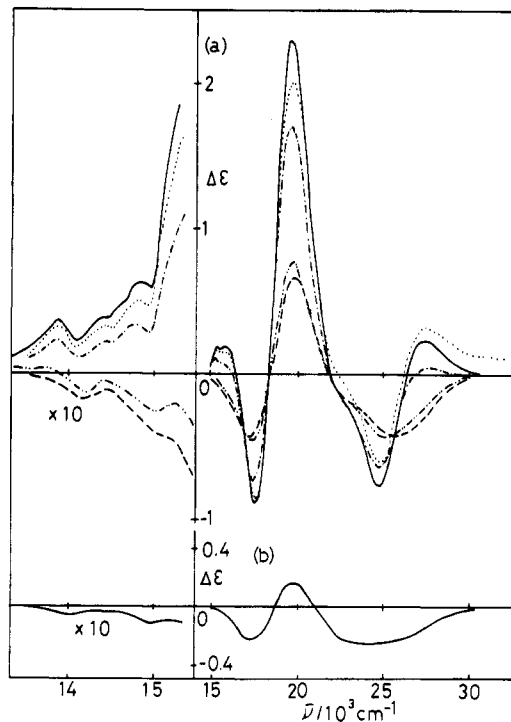(13) Kaizaki, S. *Bull. Chem. Soc. Jpn.* **1983**, 56, 3620.

Figure 1. CD spectra: (a) [Cr{(S)-pdta}]⁻ in 1 mM HClO₄ (—), in H₂O (···), in 0.01 M HClO₄ (–·–), in 0.1 M HClO₄ (–··–), and in 1 M HClO₄ (---); (b) [Cr{(S)-pdtra}(H₂O)] in 1 mM HClO₄.
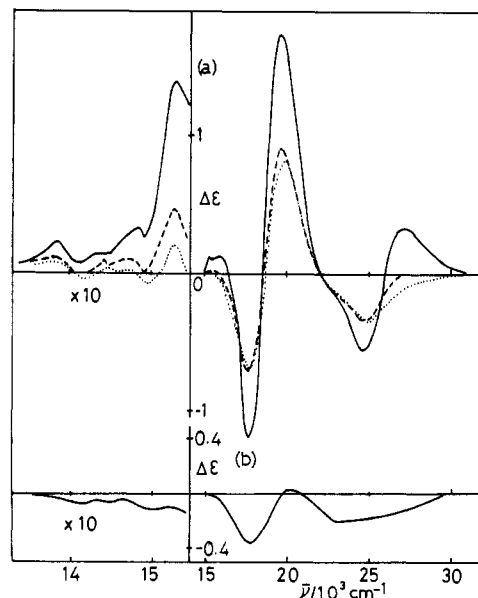

Figure 2. CD spectra: (a) [Cr{(S,S)-cydta}]⁻ in H₂O (—), in 2 M HClO₄ (---), and in 4 M HClO₄ (···); (b) [Cr{(S,S)-cydtra}(H₂O)] in 1 mM HClO₄.

The elemental analyses for the complexes concerned are summarized in Table I.

Measurements. The absorption spectra were recorded by Shimadzu UV-200S and/or UV-240 spectrophotometers. The CD spectra were measured by a Jasco MOE-1 spectropolarimeter in solutions ranging in
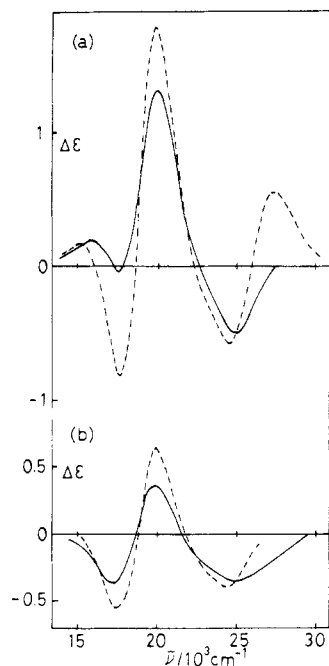
Figure 3. Solid CD spectra in Nujol mulls: (a) Na[Cr{(S)-pdta}]·3H$_2$O (—) and Na[Cr{(S,S)-cydta}]·4H$_2$O (- - -); (b) [Cr{H(S)-pdta}(H$_2$O)]·2H$_2$O (—) and [Cr{H(S,S)-cydta}(H$_2$O)]·2H$_2$O (- - -).

concentration from 5 to 7 mM (1 mM = 1 × 10^{-3} mol/dm^3) in the complexes. The quantitative solid CD spectra were obtained in the multiple-scattering systems by the Nujol mull method developed by Taniguchi and Shimura[14] with use of the above spectropolarimeter. The MCD spectra were recorded by the same spectropolarimeter as for the CD measurement in a magnetic field of 1.5 T (1 T = 1 × 10^4 G) in concentrations around 50 mM in the complexes at room temperature. The infrared spectra in D$_2$O were obtained by a Jasco IR A-3 infrared spectrophotometer with a KRS-5 solution cell.

Results and Discussion

Solution Structures. The chiroptical spectra of the edta-like complexes are shown in Figures 1–4, and their absorption data are summarized in Table II.

The (S)-pdta complex in solution gives a remarkable CD change in the d–d transition region with different acid concentrations from 1 mM to 1 M HClO$_4$, whereas identical spectra are observed in 1 and 2 M HClO$_4$, as illustrated in Figure 1a. This CD change is more evident than the absorption spectral behavior shown in Table II and the previous results for the edta complex.[1] That is, the CD intensities of two components with alternate signs at 17 600 and 19 600 cm^{-1} in the first band region of the (S)-pdta complex decrease with increasing acid concentrations. The positive CD components observed near 15 700 and 27 400 cm^{-1} in 1 mM HClO$_4$ disappear in 1 M HClO$_4$ as shown in Figure 1. In the lower frequency spin-forbidden absorption band region corresponding to the ^{2}E, ^{2}T$_1$ ← ^{4}A$_2$ transitions from 14 000 to 15 000 cm^{-1}, the CD variation is more extreme than that in the spin-allowed band region. The CD signs of all the peaks in this region are reversed with increasing acid concentrations (Figure 1a). Similar CD behavior is also observed for [Cr{(S,S)-cydta}]$^-$. The CD spectrum of this complex in water (pH 5.0) is almost identical with that of the (S)-pdta complex in 1 mM HClO$_4$ (pH 4.5), and the CD changes with the changing acid concentrations resemble those of the (S)-pdta complex (Figure 2a); the (S,S)-cydta complex in 4 M HClO$_4$ exhibits a CD spectrum similar to that of the (S)-pdta complex in 1 and 2 M HClO$_4$ except in the region of the spin-forbidden transitions, where the CD signs of only two peaks are reversed (Figure 2a). These edta-like complexes in stronger acid solutions give a CD pattern very similar to that of the (S)-pdtra and (S,S)-cydtra complexes except in the spin-forbidden transitions for the (S,S)-cydta complex (Figures 1 and 2). Thus, such an
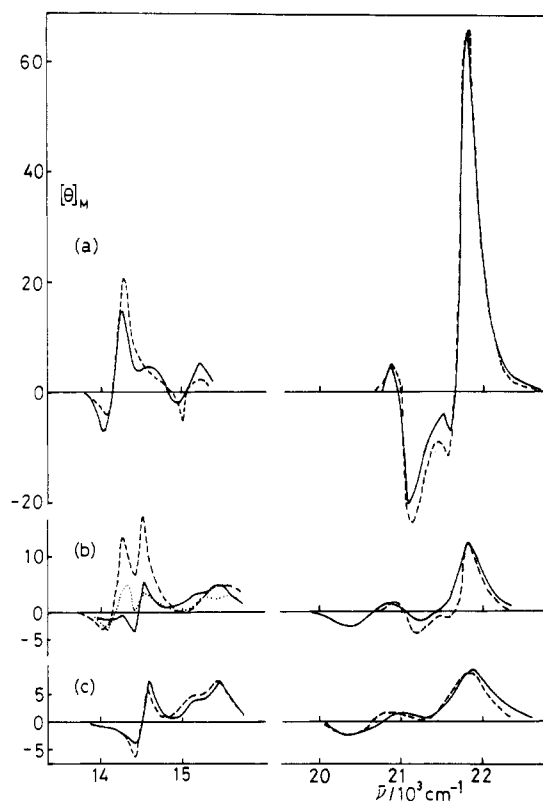
acid-dependent CD variation for the (S)-pdta and (S,S)-cydta complexes may be associated with the structural change to the edtra-like complexes, but not with the epimerization of the (S)-pdta and (S,S)-cydta complexes, since both of these complexes are formed stereospecifically[15] to take a Λ (ΛΛΛ) absolute configuration disregarding any possibility of the contamination of a negligibly small amount of the Δ (ΔΛΔ) diastereomer which has been found for the corresponding cobalt(III) complex.[16] In addition, the quantitative solid CD spectra in Nujol mulls of Na[Cr{(S)-pdta}]·3H$_2$O and Na[Cr{(S,S)-cydta}]·4H$_2$O are similar in intensity as well as in pattern to their solution CD spectra around pH 5 and analogous to the solid CD pattern of a spontaneously resolved crystal of K[Cr(edta)]·2H$_2$O in a Nujol mull.[7] In contrast, the solid CD spectra of [Cr{H(S)-pdta}(H$_2$O)]·2H$_2$O and [Cr{H(S,S)-cydta}(H$_2$O)]·2H$_2$O in Nujol mulls resemble the solution CD spectra of the (S)-pdta and (S,S)-cydta complexes in stronger acid solutions, especially in the regions near 17 600 and 27 400 cm^{-1} (Figure 3). Therefore, the sodium and the hydrogen forms of the chiral complexes could correspond to sexidentate- and quinquedentate-coordinated edta-like complexes, respectively, not only as supposed from the aforementioned acid-dependent CD behavior of the edta-like complexes but also as revealed for both forms of the complexes in crystals.[6,7,11]

The MCD behavior in the spin-forbidden transitions of [Cr(edta)]$^-$ and [Cr(rac-cydta)]$^-$ in acid solutions provides some information similar to the acid-dependent CD change of Λ-[Cr{(S)-pdta}]$^-$ and Λ-[Cr{(S,S)-cydta}]$^-$.

The MCD spectrum in the ^{2}T$_2$ ← ^{4}A$_2$ transition around 21 500 cm^{-1} as well as in the ^{2}E, ^{2}T$_1$ ← ^{4}A$_2$ region near 14 500 cm^{-1} for [Cr(Hedta)(H$_2$O)] in 0.1 M HClO$_4$ are found to be almost identical with those for [Cr(hedtra)(H$_2$O)] and for [Cr(edtra)(H$_2$O)] in 1 mM HClO$_4$ and very similar to that of [Cr-

Figure 4. MCD spectra: (a) [Cr(edta)]$^-$ (44.7 mM) in 10 mM HClO$_4$ (—) and [Cr(rac-cydta)]$^-$ in H$_2$O (- - -); (b) [Cr(Hedta)(H$_2$O)] in 0.1 M HClO$_4$ (—) and in 1 mM HClO$_4$ (···) and [Cr(rac-cydta)]$^-$ in 2 M HClO$_4$ (- - -); (c) [Cr(edtra)(H$_2$O)] (—) and [Cr(hedtra)(H$_2$O)] (- - -) in 1 mM HClO$_4$. The MCD intensities, [θ]$_M$, are in units of deg cm^{-1} dm^3 mol^{-1} T^{-1} (1 T = 10^4 G).

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(*rac*-cydta)]⁻ in 2 M HClO₄ (Figure 4b,c). [Cr(edta)]⁻ (at a concentration of 44.7 mM) in 10 mM HClO₄ at pH 5.5 and [Cr*rac*-cydta)]⁻ in H₂O at pH 5.1 give MCD spectra very similar to each other (Figure 4a). The MCD patterns of the last two complexes on the lower frequency side of the $^2E \leftarrow {}^4A_2$ transitions near 14 000 cm⁻¹, on the higher frequency side of the $^2E \leftarrow {}^4A_2$ transitions near 14 000 cm⁻¹, and on the higher frequency side of the $^2T_2 \leftarrow {}^4A_2$ transitions near 21 800 cm⁻¹ are different from those of the Hedta- and edtra-like complexes. For the edta-like complexes around pH 5, the two lowest frequency MCD peaks with opposite signs at 14 000 and 14 200 cm⁻¹ are located further to lower frequency by about 300 cm⁻¹ than those in strong acid, and the highest frequency peaks at 21 800 cm⁻¹ become several times more intense than those of [Cr(Hedta)(H₂O)] in 0.1 M HClO₄ and the *rac*-cydta complex in 2 M HClO₄ and of the related quinquedentate edtra-like complexes. New negative MCD peaks appear near 14 800 and 21 300 cm⁻¹ for the edta and *rac*-cydta complexes around pH 5. This MCD behavior suggests that the solution structure of [Cr(edta)]⁻ at pH 5.5 is almost identical with that of [Cr(*rac*-cydta)]⁻ at pH 5.1.

Meanwhile, the infrared absorption spectra in the region corresponding to asymmetric stretching vibrations of carboxyl moieties of the (S)-pdta complex in D₂O show an acid concentration dependence. Only one broad band at 1630 cm⁻¹ is observed for [Cr{(S)-pdta}]⁻ in D₂O. In 2 M DCl, however, two bands are observed at 1642 and 1720 cm⁻¹, of which the latter, higher frequency band is due to an un-ionized carboxylic acid, as found for the solid IR spectra of the Hedta-like complexes.[3] This fact also implies that the (S)-pdta complex in 2 M DCl contains a quinquedentate H(S)-pdta³⁻ ligand with a free acetic acid arm.

In view of these IR spectra as well as the similarity of the chiroptical spectra of the edtra or (S)-pdtra and (S,S)-cydtra complexes and of the edta or (S)-pdta and (S,S)-cydta complexes, the edta-like complexes in stronger acid solutions could have the same cis-equatorial configuration as [Cr(Hedta)(H₂O)] in crystals; i.e., the structure with a dangling acetic acid of the in-plane girdle (G) rings.[6] As mentioned before, in the ^2E, $^2T_1$ transitions, the chiroptical spectra of the cydta complexes in 2 or 4 M HClO₄ show some peaks corresponding to the sexidentate cydta complex in H₂O, though the spectral patterns in the spin-allowed transitions are similar to those for the edtra-like complexes (Figures 2 and 4). This fact suggests that the sexidentate species of the cydta complex remains in considerable concentration even in 4 M HClO₄, as claimed from the ^2H NMR spectra.[8b] From the IR and chiroptical spectra of the edta-like complexes in H₂O or weakly acidic solutions, on the other hand, it is most likely that the solution structure of [Cr(edta)]⁻ at pH 5.5 is the same as that of the (S)-pdta and (S,S)-cydta complexes in water or weakly acidic solutions.

There may be three possible coordination modes in solutions for the edta-like complexes: first, an octahedral coordination with a sexidentate edta; second, a pentagonal-bipyramidal seven-coordination having a water molecule between two G-ring carboxylate oxygens of the sexidentate edta as found for Rb[Fe-(edta)(H₂O)]·H₂O;[17] third, a pseudosexidentate edta octahedral coordination with an intramolecular hydrogen bond between an ionized carboxylate oxygen of a free dangling G-ring acetate of the edta⁴⁻ group and a proton of the coordinated water molecule. For the third coordination mode, it is likely that the rapid exchange of the ligating atoms (water and acetate oxygens) at the alternate sites of the G rings occurs in view of the kinetic data. Thus, any of the three possible coordination modes could explain not only the ^2H NMR spectra but also the CD enhancement for the edta-like complexes in H₂O or 1 mM HClO₄ in comparison with the CD intensities in stronger acid solutions. Unlike the case for the ^2H NMR spectra, however, the close similarity in pattern and intensity between the solution and solid CD spectra of the edta-like complexes eliminates any possibility of seven-coordination and rapid ligand atom exchange; their CD spectra are intense (Δε =

ca. ±2) enough to arise from the configurational chirality due to genuine sexidentate chelation. Further, the remarkable MCD change as one goes from [Cr(edta)]⁻ or [Cr(*rac*-cydta)]⁻ to [Cr(Hedta)(H₂O)] or [Cr{H(*rac*-cydta)}(H₂O)] may be attributable to the inherent difference in electronic properties arising from different coordination bonds rather than to the slight change caused by the hydrogen bond, since this MCD change is more notable than that due to the difference in N–O chelate ring sizes of the edta analogues.[18] Accordingly, the above solution and solid spectroscopic evidence substantiates the first mode, octahedral coordination with the sexidentate edta around pH 5, as revealed for K[Cr(edta)]·2H₂O[7] and Na[Cr(*rac*-cydta)]·4.5H₂O[11] crystals by recent X-ray analyses, and unequivocally excludes the second and the third coordination modes.

Absolute Configurations. On the basis of the present structural assignment of the edta-like complexes in solution, the CD spectra in the first spin-allowed band region may be discussed in connection with the absolute configurations of the other edta analogues. The lowest frequency positive CD component under the first band envelope near 15 900 cm⁻¹ of the (S)-pdta and (S,-S)-cydta complexes in solutions around pH 5 is ascribed to the first spin-allowed transition, not to the spin-forbidden transitions, in view of the positions and intensities. Thus, the empirical relation between the lowest frequency CD signs in the first band region and the absolute configuration holds for the present edta-like complexes as similarly found for known sexidentate edta analogues;[19] i.e., the complexes giving a positive CD component on the low-frequency side in the first band region take a Λ (ΛΛΛ) absolute configuration and vice versa. The conformity with this relation for all the sexidentate chelate edta-like complexes also suggests the formation of the sexidentate edta complexes around pH 5.

MCD Behavior. According to our previous MCD study,[18] the position of the highest frequency positive MCD peak in the spin-forbidden $^2T_2 \leftarrow {}^4A_2$ transition of the edta-like complexes depends on the chelate ring size of the N–O group in the in-plane G rings: i.e., the location of 21 700 ± 100 cm⁻¹ for six-membered rings and that of 22 300 ± 100 cm⁻¹ for five-membered rings. For the edta and *rac*-cydta complexes in solutions around pH 5, however, the highest frequency positive MCD peak is located at 21 800 cm⁻¹; this peak position being for the complexes with six-membered G rings despite the coordination of the five-membered G rings in the edta-like complexes. This may be due to severe distortion of the ligating atoms from octahedral apices as revealed by the X-ray analyses.[7,11] Such a distortion could give rise to a decrease in the tetragonal splitting of the t_{2g} orbital ($\Delta(t_{2g})$) owing to the increase in the σ-bond interaction between the metal $d_\pi(t_{2g})$ orbital and the ligand σ orbitals within the O–N–O plane as elucidated in terms of the angular overlap model (AOM).[18] Thus, the lower frequency shift of the highest frequency $^2T_2 \leftarrow {}^4A_2$ transition is expected to occur as similarly observed for the edta-like complexes with six-membered N–O G rings, where the Cr–O π interaction is considered to be predominant. The preliminary AOM calculations involving all configurational interactions for the d³ configuration were performed on the basis of the structural parameters obtained from the X-ray analyses. The numerical results approximate to the MCD positions as expected from qualitative considerations. This observation is again consistent with the present assignments of the solution structure.

Conclusions

The chiroptical evidence for the solution structure of the edta-like complexes lends more decisive support to the sexi- or quinquedentate edta coordination in solution than the ^2H NMR studies. Moreover, it has been revealed that the chiroptical spectra in the spin-forbidden transitions of chromium(III) complexes can be more sensitive to and of more diagnostic use for the stereochemistry than those in the first spin-allowed transitions as pursued

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Single-Crystal Polarized Electronic Absorption Spectra and Ligand Field Parameters for Triphenylphosphine and Triphenylarsine in PtCl₃L⁻ Complexes

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The single-crystal polarized electronic absorption spectra of (Pr₄N)[PtCl₃PPh₃] and (Pr₄N)[PtCl₃AsPh₃] taken at 10 K are reported. Spin-allowed and spin-forbidden ligand field transitions and a ligand-localized transition are assigned. The σ and π interactions of the triphenylphosphine and triphenylarsine ligands with the metal d orbitals are obtained by using two methods. First, the trends in the σ and π interactions are determined from trends in the energies of spectral features. Second, full-matrix angular-overlap ligand field theory calculations including spin–orbit coupling are reported and the AOM σ and π parameters are reported. The two-dimensional spectrochemical series is discussed. Triphenylphosphine is a better σ donor and a poorer π acceptor than triphenylarsine. These two ligands are compared to other ligands of interest in organometallic chemistry.

The experimental determination of the individual σ and π components of the interaction of phosphine and arsine ligands with transition metals and the comparisons of these properties with those of other important ligands in organometallic chemistry are rare. Although the σ and π interactions can be determined from transition energies measured from electronic absorption spectra and interpreted by using the angular-overlap theory, such studies are in practice inhibited by three factors. First, the d–d transitions in complexes containing phosphine and arsine ligands are usually high in energy and are obscured by more intense charge-transfer bands. Second, the extinction coefficients are frequently large, thus preventing single-crystal polarized absorption spectra from being obtained and definitive assignments from being made. Finally, in complexes where the above limitations can be overcome (e.g. tetrahedral cobalt(II) and nickel(II) triphenylphosphine complexes), detailed and definitive information about triphenylphospine was obtained but could not be compared with properties of other ligands of organometallic interest because of the limited number of complexes that can be prepared.

The most detailed information determined by electronic absorption spectroscopy about the σ and π properties of triphenylphosphine has been obtained by Gerloch et al. from tetrahedral Co(II) and Ni(II) complexes.[1-5] Triphenylphosphine was found to be a good σ donor (stronger than halides but slightly poorer than a tertiary amine) and a good π acceptor (stronger than quinoline and halides). Very little is known about the properties of arsine ligands. Studies of das (bis[o-phenylene-bis(dimethylarsine)]) have shown that its Dq values in Fe(II) and Cr(III) complexes are similar to those for ethylenediamine.[6] The σ and π properties, obtained from a series of halide complexes of the form Fe(das)₂XY⁺, showed that das is a slightly better σ donor than ethylenediamine and a better π acceptor than halides.[7]

A series of compounds that is proving to be amenable to detailed study of the σ and π interactions of ligands of organometallic importance is the PtCl₃L^{n-} series where L can range from "Werner" ligands such as amines, halides, and pseudohalides to ligands of organometallic interest such as olefins, carbenes, CO, phosphines, and arsines.[8-17] The problem of large extinction coefficients has been overcome by using new microspectroscopic techniques that allow polarized electronic spectra of crystals to be obtained even when $\epsilon > 10^3$ mol⁻¹ L cm⁻¹.[15,18] Because only the ligand L changes in the series, systematic changes in the σ and π properties of the ligand are accurately measured and interpreted.

We report here spectroscopic results for [PtCl₃PPh₃]⁻ and [PtCl₃AsPh₃]⁻. The single-crystal polarized electronic absorption spectra at 10 K, the assignments of the bands, and the angular-overlap σ and π parameters are reported. The σ and π interactions of the ligands with the metal are determined by using two methods. First, the relative trends in the σ interactions, the π interactions, and the covalency (nephelauxetic effect) are determined directly from the trends in the energies of the spectroscopic features. Second, the complete AOM matrix calculation including spin–orbit coupling is reported and the positions of the ligands in the two-dimensional spectrochemical series are discussed.

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