Syntheses. $[C_5H_5Mo(CO)S_2C_6H_3(CH_3)]_2$. $[C_5H_5Mo(CO)_3]_2$ (2.3 g, 4.7 mmol) and 3,4-dimercaptotoluene (1.5 g, 9.6 mmol) were refluxed in 50 mL of methylcyclohexane under nitrogen for 18 h to form a dark purple solution. The solvent was removed by rotoevaporation, and the resulting solid was chromatographed without protection from air on a 2.5 × 25 cm column. Elution with benzene gave first a minor green fraction ($[C_5H_5MoS_2C_6H_3(CH_3)]_2$) and then the purple product. The solvent was removed and the sample was dried in vacuo for 12 h; yield 2.7 g, 84%. Anal. Calcd for $C_{26}H_{22}O_2S_4Mo_2$: C, 45.58; H, 3.23; S, 18.68. Found: C, 45.54, H, 3.43; S, 18.62. Yield of $[C_5H_5MoS_2C_6H_3(CH_3)]_2$: 0.3 g, 10%.

$[C_5H_5MoS_2C_6H_3(CH_3)]_2$. $[C_5H_5Mo(CO)S_2C_6H_3CH_3]_2$ (0.69 g, 1.0 mmol) was photolyzed with a Hanovia 450-W Hg arc lamp in a quartz submersible well in 350 mL of toluene for 3.5 h. The resulting green solution was rotoevaporated to dryness, and the solid was washed with acetone to remove any remaining starting complex; yield 0.47 g, 74%. Anal. Calcd for $C_{24}H_{22}S_4Mo_2$: C, 45.71; H, 3.52; S, 20.33. Found: C, 45.85; H, 3.58; S, 20.35.

$C_5H_5Mo(CO)_2S_2CC_6H_5$ and $[C_5H_5Mo(S)S_2CC_6H_5]_2$. $[C_5H_5Mo(CO)_3]_2$ (1.0 g, 2.0 mmol) and $Zn(S_3CC_6H_5)_2$ (0.87 g, 2.0 mmol) were refluxed under nitrogen in 50 mL of benzene for 20 h. The purple solution was filtered in air; the resulting brown precipitate was washed with CH_2Cl_2 until washings were colorless and then discarded. The filtrate was evaporated to dryness. Addition of 75 mL of diethyl ether dissolved the red purple complex $C_5H_5Mo(CO)_2S_2CC_6H_5$. The ether solution was filtered and evaporated; the monomeric product was further purified by column chromatography eluting with 10:1 hexanes/CH_2Cl_2; yield 0.74 g, 49%. Anal. Calcd for $C_{14}H_{10}O_2S_2Mo$: C, 45.40; H, 2.72; S 17.32. Found: C, 45.54; H, 2.82; S, 17.17. The black ether-insoluble product was recrystallized from CH_2Cl_2 and found to be $[C_5H_5Mo(S)S_2CC_6H_5]_2$; yield 0.34 g, 24%. Anal. Calcd. for $C_{24}H_{20}S_6Mo_2$: C, 41.62; H, 2.91; S, 27.77. Found: C, 41.44; H, 2.98; S, 27.60.

Photolytic Reaction of $C_5H_5Mo(CO)_2S_2CC_6H_5$ with Sulfur. The monomeric complex (0.71 g, 1.9 mmol) and sulfur (0.36 g, 1.4 mmol) were photolyzed under nitrogen in the apparatus described above in 350 mL of toluene for 2 h. $[C_5H_5Mo(S)S_2CC_6H_5]_2$ was isolated by using the procedure described above; yield 0.28 g, 43%. No reaction was observed when toluene solutions of the monomeric complex were refluxed under nitrogen with excess sulfur for 48 h.

$C_5H_5Mo(S_2CC_6H_5)(S_2C_6H_3(CH_3))$. $C_5H_5Mo(CO)_2S_2CC_6H_5$ (0.51 g, 1.4 mmol) and 3,4-dimercaptotoluene (0.11 g, 0.70 mmol) were photolyzed under nitrogen in the apparatus described above in 400 mL of toluene for 3 h. The solvent was removed by rotoevaporation, and the residue was chromatographed with a 4:1 toluene/hexanes solution to give the red product; yield 0.11 g, 35%. Anal. Calcd. for $C_{19}H_{16}S_4Mo$: C, 48.72; H, 3.42; S, 27.35. Found: C, 48.88; H, 3.56; S, 27.26.

Attempted Reactions of $[C_5H_5Mo(CO)S_2C_6H_3(CH_3)]_2$ with an Isocyanide. The molybdenum complex (0.10 g, 0.14 mmol) and excess *n*-butyl isocyanide (0.4 mmol) were refluxed in $CHCl_3$ for 6 days. The starting complex was recovered and identified by IR and NMR spectra.

Acknowledgment. Support for this work from the donors of the Petroleum Research Fund, administered by the American Chemical Society, from the National Science Foundation, and, in part, from the Department of Energy, Office of Basic Energy Sciences, and the University of Colorado Computing Center is gratefully acknowledged.

Registry No. I, 86885-25-8; II, 86885-24-7; III, 86885-22-5; IV, 86885-23-6; V, 86885-26-9; $C_5H_5Mo(S_2CC_6H_5)[S_2C_6H_3(CH_3)]$, 86900-63-2.

Supplementary Material Available: Complete listings of bond lengths and angles, tables of thermal parameters, and tables of observed and calculated structure amplitudes (96 pages). Ordering information is given on any current masthead page.

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Crystal Structure and Low-Temperature Crystal Spectra of Dicesium *trans*-Dichlorotetraaquotitanium(III) Chloride

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$Cs_2TiCl_5\cdot 4H_2O$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 9.565$ (1) Å, $b = 9.3077$ (8) Å, $c = 9.2813$ (8) Å, $\beta = 116.44$ (1)°, and $Z = 2$. The structure was refined by full-matrix least squares to $R = 0.048$ for 1205 reflections having $I > 3\sigma(I)$ and $2\theta < 50°$. The crystals contain *trans*-$[TiCl_2(H_2O)_4]^+$ ions that lie on crystallographic centers of symmetry. The Ti–Cl, Ti–O(1), and Ti–O(2) distances are 2.400 (2), 2.033 (5), and 2.046 (6) Å, respectively. The Cs^+ ions are coordinated to eight chloride ligands at the corners of a distorted square antiprism; the average Cs–Cl distance is 3.62 (1) Å. The optical spectra that originate from the ^2E_g (D_{4h}) ground state are vibronic in nature; the σ spectrum is much weaker than the π. The tetragonally split ^2E_g (O_h) yields excited states at 14 970 ($^2A_{1g}$) and 19 220 ($^2B_{1g}$) cm^{-1}. The upper band has a shoulder 2640 cm^{-1} above the peak; this is due to coupling of a water vibration with the ligand field transition.

Introduction

Many halo–aquo complexes of the first-row transition metals contain the *trans*-dihalotetraaquometal chromophore.[2] Recently we reported the structure and spectra of $Cs_2CrCl_5\cdot 4H_2O$[2] and $Cs_3VCl_6\cdot 4H_2O$,[3] both of which contain this chromophore. Here we extend the study to be titanium(III) analogue, $Cs_2TiCl_5\cdot 4H_2O$. This compound forms large crystals

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(1) (a) Canisius College. (b) Brock University.

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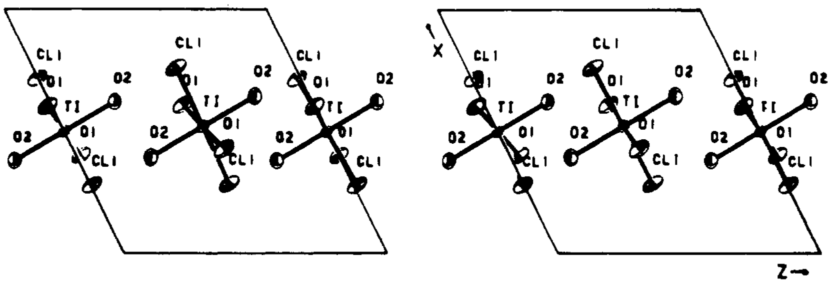

Figure 1. ORTEP drawing[10] of the $[TiCl_2(H_2O)_4]^+$ chromophores in the unit cell. The view is a projection onto the (010) plane.

that are excellent for optical spectroscopy.

$TiCl_3 \cdot 6H_2O$ has been shown to have the same powder X-ray pattern as $VCl_3 \cdot 6H_2O$, which contains the *trans*-$[VCl_2(H_2O)_4]^+$ chromophore.[4] Earlier Schläfer and Fritz[5] had concluded from reflectance spectra and IR measurements that $TiX_3 \cdot 6H_2O$ (X = Cl or Br) must contain the *trans*-dihalotetraaquotitanium(III) ion. As expected, we found the same chromophore in $Cs_2TiCl_5 \cdot 4H_2O$.

Experimental Section

Preparation of the Compound. $Cs_2TiCl_5 \cdot 4H_2O$ was prepared by dissolving stoichiometric amounts of anhydrous $TiCl_3$ (Research Inorganic Chemicals (RIC), 98% purity) and CsCl (RIC, 99% purity) in a minimum amount of 2 M HCl. The solution was allowed to evaporate over concentrated H_2SO_4 in a desiccator filled with N_2 or Ar. Large, strongly dichroic plates separated in about a day. Under polarized light they are red-violet in one direction and nearly colorless in the orthogonal direction. While the crystals are fairly stable when they are dry and are out of contact with oxygen, even under these conditions the crystal surface slowly becomes covered with a white powder. After long standing (several months) the powder is seen to be pale green. Dehydration and/or oxidation of Ti(III) appears to be taking place.

If, after the large crystals are removed, the original solution is evaporated further, some small green crystals appear. These may be $Cs_2TiCl_5 \cdot H_2O$. Green crystals of this composition can be prepared at 0 °C in a solution saturated with HCl;[6] they were first reported by Stähler.[7]

Ti was determined by addition of excess standard $KMnO_4$ to the sample. Then a weighed amount of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ was added, and excess Fe(II) was titrated with $KMnO_4$. Anal. Calcd for $Cs_2TiCl_5 \cdot 4H_2O$: Ti, 8.51. Found: Ti, 8.66.

Spectra. Polarized crystal spectra were recorded at room temperature and at about 10 K on a Cary 14 spectrophotometer equipped with a Displex cryogenic refrigerator. The electric vector of the light was aligned along extinction axes of the crystal.

X-ray Structural Determination. A large single crystal was cut apart, and a small irregular fragment (ca 0.1 × 0.15 × 0.3 mm) was mounted on a thin glass fiber. The crystal was transferred to an Enraf-Nonius CAD-4 automated single-crystal diffractometer. Graphite-monochromatized Mo Kα radiation ($\lambda(\alpha_1)$ = 0.709 26 Å) was used to determine the cell dimensions from 21 accurately centered reflections with $11° < \theta < 21°$: a = 9.565 (1) Å, b = 9.3077 (8) Å, c = 9.2813 (8) Å, β = 116.44 (1)°. The data collection conditions were as follows: ω–2θ scan, ω-scan width $(0.80 + 0.35 \tan \theta)°$, $\theta_{min} = 2°$, $\theta_{max} = 25°$, 3-mm aperture, maximum ω-scan speed 10° min^{-1}, maximum scan time 300 s, background counted one-fourth of the scan time at each end of the scan. A standard was measured every hour and the orientation checked after every 50 measured reflections. Two quadrants of data were measured. The equivalences, $I(hkl) = I(h\bar{k}l)$, established the symmetry as monoclinic, and the systematic absences ($h0l$ absent for odd l, $0k0$ absent for odd k) led to the assignment of space group $P2_1/c$.

Table I. Fractional Coordinates for $Cs_2TiCl_5 \cdot 4H_2O^a$

atom	x	y	z
Cs	0.09818 (6)	0.05676 (6)	0.26603 (6)
Ti	0.5	0.5	0.5
Cl(1)	0.2780 (3)	0.3810 (2)	0.5015 (3)
Cl(2)	0.1221 (2)	−0.2802 (2)	0.0616 (3)
Cl(3)	0.5	0.0	0.5
O(1)	0.4069 (7)	0.6903 (6)	0.5220 (8)
O(2)	0.3801 (7)	0.5147 (8)	0.2549 (7)

[a] In this and the following tables, the estimated standard deviation in the final digits is given in parentheses.

Table II. Some Important Distances (A) and Angles (deg) in $Cs_2TiCl_5 \cdot 4H_2O^a$ (Esd's in Parentheses)

Ti–O(1)	2.033 (5)	Cs–Cl(1)	3.674 (2)
Ti–O(2)	2.046 (6)	Cs–Cl(1)^{iv}	3.617 (2)
Ti–Cl(1)	2.400 (2)	Cs–Cl(1)^{vii}	3.719 (2)
O(1)···Cl(2)^{iii}	3.025 (6)	Cs–Cl(2)	3.724 (2)
O(1)···Cl(3)^{ii}	3.051 (6)	Cs–Cl(2)^{i}	3.508 (2)
O(2)···Cl(2)^{ii}	3.002 (6)	Cs–Cl(2)^{v}	3.695 (2)
O(2)···Cl(3)^{iv}	3.058 (6)	Cs–Cl(2)^{vi}	3.507 (2)
		Cs–Cl(3)	3.512 (1)
O(1)–Ti–O(2)	90.3 (3)	Cl(1)–Cs–Cl(2)^{v}	105.84 (5)
Cl(1)–Ti–O(2)	88.7 (2)	Cl(3)–Cs–Cl(2)^{vi}	119.83 (5)
Cl(1)–Ti–O(1)	88.5 (2)	Cl(2)–Cs–Cl(2)^{i}	101.95 (7)
		Cl(1)^{iv}–Cs–Cl(1)^{vii}	103.20 (7)

[a] Symmetry superscripts: none (x, y, z); i $(-x, -y, -z)$; ii $(x, 1 + y, z)$; iii $(x, 0.5 - y, 0.5 + z)$; iv $(x, 0.5 - y, -0.5 + z)$; v $(x, -0.5 - y, 0.5 + z)$; vi $(-x, 0.5 + y, 0.5 - z)$; vii $(-x, -0.5 + y, 0.5 - z)$.

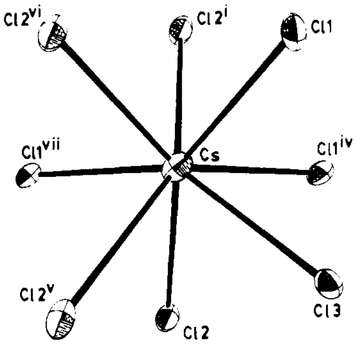

Figure 2. The coordination polyhedron of Cs^+.

Intensities were corrected for background and variations in the standard and converted to structure factors after applying Lorentz and polarization corrections. Symmetry-equivalent reflections were averaged. No absorption correction was applied (μ = 64.2 cm^{-1}).

The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques with the SHELX set of programs.[8] Scattering factors for neutral Cs, Ti, Cl, and O atoms were taken from ref 9. The function minimized was $\sum w\Delta^2$, where $\Delta = |F_o| -$

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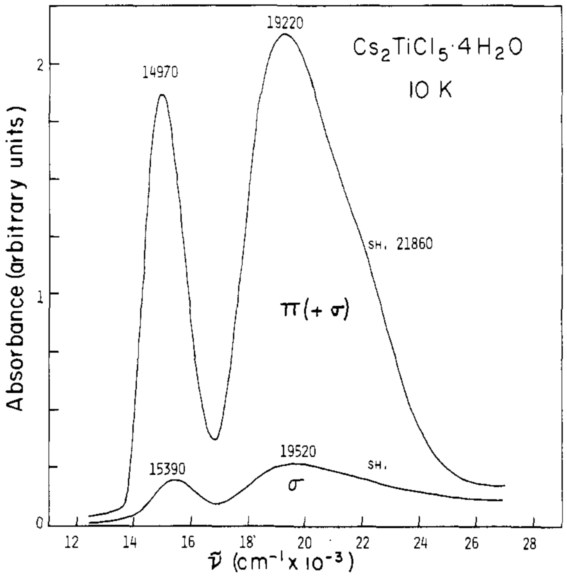

Figure 3. Polarized crystal spectra at 10 K of $Cs_2TiCl_5{\cdot}4H_2O$. The weaker spectrum is σ, and the stronger is 78.5% π + 21.5% σ.

$|F_c|$, $w = (\sigma^2(F_o) + 0.0001F_o^2)^{-1}$, and $\sigma(F_o)$ is the standard deviation based on counting statistics. The final R and R_w were 0.048 and 0.046, respectively, for the 1205 reflections having $I > 3\sigma(I)$, and 0.052 and 0.046, respectively, for all 1292 reflections. The final difference map showed several peaks of 1 e Å^{-3}, but none were assignable to hydrogen atoms. Tables of the observed and calculated structure factors are available (see paragraph on supplementary material).

Results

X-ray Crystal Structure. The final atomic coordinates and thermal parameters for $Cs_2TiCl_5{\cdot}4H_2O$ are given in Table I, and the important distances and angles are listed in Table II. The Ti(III) ions lie on crystallographic centers of symmetry, and the chromophore is *trans*-$[TiCl_2(H_2O)_4]^+$. The formula of the compound is thus $Cs_2[TiCl_2(H_2O)_4]Cl_3$. The distribution of the $[TiCl_2(H_2O)_4]^+$ ions in the unit cell is shown in Figure 1. The cesium coordination polyhedron is presented in Figure 2.

Absorption Spectra. The polarized crystal spectra of the complex in the visible region at 10 K are shown in Figure 3. The spectra were recorded with the light incident on the *ac* (010) plane of the crystal; this was confirmed by an X-ray precession photograph. Under crossed polarizers one of the extinction axes of this plane lies about 87° from the *a* crystal axis. Since the O(2)–Ti–O(2) axis of the chromophore makes an angle of 86.2° with the *a* axis, the spectrum recorded with light polarized along this extinction axis (the weaker spectrum) is almost pure σ (σ and π polarizations have the electric vector of light perpendicular and parallel to C_4, respectively). The orthogonal polarization has the electric vector of light nearly parallel to the plane containing the Cl–Ti–Cl axes. However, because these axes alternate in orientation in adjacent chromophores (Figure 1) and make an angle of 27.6° with the (010) plane, this polarization is about 78.5% π and 21.5% σ.

In both spectra the bands shrink noticeably as the crystal is cooled. The bands in both polarizations also show the usual shift to higher energy as the crystal is cooled. This latter effect is due to depopulation of the low-energy levels of the ground state upon cooling.

The maxima in the two polarizations at 10 K are not exactly the same; this will be commented on below. In the strong polarization the lower energy band shows well-developed fine structure on its low-energy side. This is being further investigated and will be reported later.[11] Finally, in both polarizations at low temperature a shoulder is seen on the high-energy side of the upper band. This appears to be analogous to similar bands observed in the spectra of aquo–halo complexes of Cr(III),[2] V(III),[3] and Co(II).[12]

Discussion

X-ray Crystal Structure. The $TiCl_2O_4$ moiety nearly has D_{4h} symmetry, as shown by the distances and angles in Table II. The pseudo-C_4 axis of each complex, Cl(1)–Ti–Cl(1), is aligned almost exactly parallel to the (001) planes; the intersection angle is 0.3° (Figure 1). The O(2)–Ti–O(2) axis, when projected onto the (010) plane, makes an angle of 3.8° with the normal to the (001) planes. This direction corresponds within experimental error to the direction of the weak polarization in the spectrum.

The cesium ions are coordinated to eight chloride ions with distances ranging from 3.507 to 3.724 Å (Table II). The coordination polyhedron is a distorted square antiprism (Figure 2), with an elongation in the direction of the pseudo-S_8 axis. This geometry is one of the usual ones for $[M(\text{monodentate})_8]^{n+}$ complexes.[13]

Each of the water molecules forms moderately strong hydrogen bonds to two chloride ions (Table II) so that the chromophore is involved in eight such linkages. The O···Cl distances of 3.002 (6)–3.058 (6) Å compare favorably with the value of 3.1 Å cited for typical O–H···Cl hydrogen bonds.[14]

Furthermore, each of the Cl(1) ions in the $[TiCl_2(H_2O)_4]^+$ chromophore is bonded to two Cs^+ ions so that the structure is rigidly linked in all three directions. The main structural features of $Cs_2TiCl_5{\cdot}4H_2O$ are thus similar to those in $Cs_2CrCl_5{\cdot}4H_2O$.[2]

Crystal Spectra. The spectra can be interpreted in terms of D_{4h} symmetry. In D_{4h} the $^2T_{2g}$ (O_h) ground state becomes ^2E_g + $^2B_{2g}$ and the ^2E_g (O_h) excited sate becomes $^2A_{1g}$ + $^2B_{1g}$. The presence of two chlorines along C_4 is equivalent to axial elongation of an octahedron of six equal ligands, since Cl^- is lower than H_2O in the spectrochemical series. This would make ^2E_g the ground state in D_{4h} and yield the excited state ordering $^2A_{1g} < {}^2B_{1g}$. A ^2E_g ground state is the opposite of that proposed by Schläfer and Fritz.[5] The 4250-cm^{-1} separation of the two principal bands is a measure of the tetragonal splitting caused by the two ligand sets.

In this centrosymmetric complex the coupling of u vibrations to the excited g electronic states is the expected mechanism by which the forbidden electronic transitions acquire their intensity. This expectation is confirmed by the fact that the absorption bands decrease in area as the crystal is cooled. In both polarizations the areas of the 14 970- and 19 220-cm^{-1} bands at 10 K are about 40% and 75%, respectively, of their room-temperature values.

Vibronic selection rules indicate that from the ^2E_g ground state transitions to *both* excited states are vibronically allowed in σ by coupling with a_{2u} or b_{2u} vibrations and in π by coupling with e_u vibrations. Of the 15 normal vibrations of the $TiCl_2O_4$ chromophore, the u vibrations with the assignments for $Cs_2TiCl_5{\cdot}4H_2O$ are as follows. e_u: ν(Ti–O), 506 cm^{-1}; δ(TiO_4 in plane), 265 cm^{-1}; δ(Cl–Ti–Cl), 142 cm^{-1}. a_{2u}: ν(Ti–Cl), 328 cm^{-1}; δ(TiO_4 out of plane), 245 cm^{-1}. b_{2u}: δ(TiO_4 out-of-plane), IR inactive (calcd 204 cm^{-1}). All data are from ref 15 except 142 cm^{-1}, which was taken from ref 5 for $TiCl_3{\cdot}6H_2O$. The symmetry of the ground state is confirmed by the

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group-theoretical calculations showing that from a $^2B_{2g}$ ground state transitions would be vibronically allowed only in σ; no π-vibronic spectrum would be had, since there are no a_{1u} or b_{1u} vibrations of the chromophore $TiCl_2O_4$.

In terms of orbital angular-overlap parameters, the proposed energy-level scheme suggests that e_σ' and e_π' for oxygen are greater than the corresponding parameters for chlorine. The order of the σ parameters is that expected from the spectrochemical series. While the ordering of the π values is less evident, it agrees with that found for the analogous Cr(III) complex[2] and that proposed earlier by Barton and Slade.[16]

It may be worth noting that in the spectra of the three complexes, $Cs_2TiCl_5\cdot4H_2O$, $Cs_2CrCl_5\cdot4H_2O$,[2] and $Cs_3VCl_6\cdot4H_2O$,[3] the π spectrum is the stronger in each case. The dichroism is the strongest in the titanium complex and weakest in the chromium complex.

The band that appears as a shoulder 2640 cm^{-1} above the 19 220-cm^{-1} band is most probably due to the coupling of an O–H stretching vibration with the ligand field transition. This vibration notriceably couples only with the upper ligand field state $^2B_{1g}$. In the spectra of some crystals there appears to be one or two other components closer to the band maximum. The distances from the maximum are in the range of other water vibrations. So it may be that more than one water vibration is involved in this shoulder. In the analogous chromium and vanadium complexes a similar band appeared associated also with only one of the ligand field bands, but the symmetry of the bands could not be uniquely determined. The separations in the vanadium and chromium complexes were 2890 and 3070 cm^{-1}, respectively.[2,3]

The difference in maxima in the two polarizations is probably related to the differences in the magnitude of the u vibrations that produce the vibronic bands in the two polarizations.

The ground state ^2E_g will be subject to Jahn–Teller distortion. In D_{4h}' this will become the two Kramers doublets, $E_{1/2g}$ and $E_{3/2g}$; the magnitude and order of this splitting are not known. But the selection rules indicate that transitions to all excited spin–orbit states are vibronically allowed from each ground-state component in both polarizations. So the introduction of spin–orbit coupling will not alter the above arguments.

An attempt was made to fit the observed spectra to the energies calculated for d^1 in D_{4h} symmetry. From the best fit obtained for $Cs_2CrCl_5\cdot4H_2O$,[2] we were able to assign the spectra of $Cs_3VCl_6\cdot4H_2O$[3] by using the same values of the tetragonal parameters, Ds and Dt. Calculation of the energies of the present compound using these same values ($Ds = 239$ and $Dt = 22$ cm^{-1}) proved unsuccessful. The tetragonal splitting is calculated to be only 1066 cm^{-1} as compared with the observed value of 4250 cm^{-1}. In the absence of further data, as for example the splitting of the $^2T_{2g}$ (O_h) ground state, no meaningful calculations can be made, since all tetragonal d^1 formulations contain more than two parameters.

Acknowledgment. P.J.M. is grateful to the Research Corp. for a grant for the purchase of the Displex cryogenic refrigerator. M.F.R. thanks the Natural Sciences and Engineering Research Council for operating and equipment grants and is especially grateful to the Atkinson Charitable Foundation and the J. P. Bickell Foundation for grants toward the purchase of the CAD-4 diffractometer.

Registry No. $Cs_2[TiCl_2(H_2O)_4]Cl_3$, 86941-16-4.

Supplementary Material Available: Listings of observed and calculated structure factors and anisotropic thermal parameters and an overall packing diagram (9 pages). Ordering information is given on any current masthead page.

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Electronic Structure of Metalloporphyrins. 2.[1] Experimental Electron Density Distribution of (*meso*-Tetraphenylporphinato)iron(III) Methoxide

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The crystal structure and experimental electron density distribution of (*meso*-tetraphenylporphinato)iron(III) methoxide, $C_{45}H_{31}N_4OFe$, has been determined from high-resolution single-crystal X-ray diffraction measurements at 100 K. Integrated X-ray intensities were collected with use of Nb-filtered Mo Kα radiation to a resolution of $(\sin\theta)/\lambda = 1.15$ Å^{-1}. Averaging 18 142 symmetry-equivalent reflections from two crystals yielded a set of 8033 independent reflections, which were refined by conventional least-squares to $R = 4.4\%$, $R_w = 5.4\%$. The iron atom is five-coordinate with the oxygen atom of the methoxide ion coordinated in the axial position at a distance of 1.816 (2) Å. The iron is displaced 0.48 Å from the plane of the four nitrogens and 0.56 Å from the mean porphyrin plane. The O–C bond of the methoxide is eclipsed with respect to one of the Fe–N bonds. The experimental electron distribution was determined by least-squares refinement including multipole deformation functions ($R = 2.3\%$, $R_w = 2.8\%$). Populations of the deformation functions in the carbon atoms of the porphyrin ligand agree well with those found previously in (*meso*-tetraphenylporphyrinato)cobalt(II), which suggests transferability of ligand density between complexes. An approximately spherical electron distribution is found at the iron site, and experimental d-orbital occupancies calculated for the iron atom from the deformation populations are consistent with a high-spin Fe(III) state. However, small but significant deviations from spherical symmetry are observed which, together with observed net atomic charges, have been used to calculate a Mössbauer quadrupole splitting constant of +0.6 (3) mm/s.

Introduction

The intense attention that has been devoted to the stereochemistry and electronic structure of metalloporphyrins results from their wide utilization in biological systems. Iron porphyrins have attracted special interest because of their use as a prosthetic group in many proteins, including myoglobin and hemoglobin. For example, in the cooperative binding of dioxygen in hemoglobin, changes both in the electronic structure and in the stereochemistry at the iron site appear to be responsible for the unique biological behavior, and the detailed mechanism is still not fully understood.[3]

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[1] Part 1: Stevens, E. D. *J. Am. Chem. Soc.* **1981**, *103*, 5087.

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