This is most likely due to the fact that λ is too large to use only second-order perturbation theory. For symmetry D_{4d} it can be shown that

$$g_{\parallel} = 2.0023 \cos 2\alpha + 2k \sin^2 \alpha$$

$$g_{\perp} = 2.0023 \cos^2 \alpha + \sqrt{6}k \sin 2\alpha$$

$$A = P\left[-\kappa + \frac{4}{7} + \frac{8}{7} \sin^2 \alpha - \frac{\sqrt{6}}{7} \sin 2\alpha\right]$$

$$B = P\left[-\kappa - \frac{2}{7} - \frac{4}{7} \sin^2 \alpha + \frac{15}{14} \sqrt{6} \sin 2\alpha\right] \quad (5)$$

$$\tan 2\alpha = -\frac{\sqrt{6}\eta}{1 - \frac{1}{2}\eta}$$

$$\eta = \frac{\lambda}{E(xz, yz) - E(3z^2 - r^2)}$$

$$\sqrt{6}k = (d_1 |l_+| d_0)$$

where an attempt to take into account covalent binding is made by allowing k to be less than 1 (its value for a pure d orbital).

Values of P, k, and κP are given in Table II along with values obtained for Mo^{5+} in other environments. For Mo^{5+} in TiO_2 and $(NH_4)_2InCl_5{\cdot}H_2O$ eq 3 was used and eq 5 was used for Mo^{5+} in $CaWO_4$ since this appears to be another case where $d_{3z^2-r^2}$ is the ground state. In the calculations it was assumed that A and B were both positive for $Mo^{95,97}$ since g_N is negative for these isotopes. The rather small values of k indicated the inadequacy of trying to represent the effects of covalency by the method employed in eq 5. Since P is proportional to $\langle r^{-3}\rangle_{av}$ the smaller value for $Mo(CN)_8{}^{3-}$ must mean that the unpaired electron is more delocalized, hence more covalent in bonding orbitals, than it is for Mo^{5+} in TiO_2 and $(NH_4)_2InCl_5{\cdot}H_2O$. The small value for $CaWO_4$ is most likely the result of a +5 ion occupying the site of the smaller +6 ion. The smaller magnitude of κP could also mean more delocalization but it could also be due to a small amount of hybridization of 5s with the $4d_{3z^2-r^2}$ orbital since this is allowed in D_{4d} symmetry. Such hybridization makes a negative contribution to κ and hence would reduce the magnitude of κP. Similar comparisons are difficult to make for W^{5+} since less data are available on the esr of W^{5+} compounds. Garifyanov, *et al.*,[18] have reported that $A = 146 \times 10^{-4}$ cm^{-1} for $WO(SCN)_5{}^{2-}$, and if it assumed that κ is similar to that in Mo^{5+} compounds then $P \sim 90 \times 10^{-4}$ cm^{-1}, which is considerably larger than that found for $W(CN)_8{}^{3-}$.

TABLE II

VALUES FOR k, P, AND κP FOR Mo^{5+} AND W^{5+}

Ion		k	P(10^{-4} cm^{-1})	κP(10^{-4} cm^{-1})
Mo^{5+} in TiO_2[a]			−44.0	−33.0
Mo^{5+} in $(NH_4)_2InCl_5{\cdot}H_2O$[b]			−48.2	−44.0
Mo^{5+} in $CaWO_4$[c]	Mo^{95}	0.32	−26.0	−24.6
	Mo^{97}	0.32	−26.9	−25.4
$Mo(CN)_8{}^{3-}$		0.08	−24.3	−28.6
$W(CN)_8{}^{3-}$		0.07	38.5	42.9

[a] See ref 14 and 15. [b] See ref 16. [c] G. H. Azarbayejani and A. L. Merlo, *Phys. Rev.*, **A137,** 489 (1965).

The fact that $g_{\parallel} < g_{\perp}$ for $Mo(CN)_8{}^{3-}$ and $W(CN)_8{}^{3-}$ when present in $K_4Mo(CN)_8$ and $K_4W(CN)_8$ suggests that d_{xy} is the ground state. This is consistent with the duodecahedral structure that would be expected in the crystal state since $Mo(CN)_8{}^{4-}$ in $K_4Mo(CN)_8{\cdot}2H_2O$ possesses this structure.[2] It has been found[19,20] that $g_{\parallel} < g_{\perp}$ for Cr^{5+} in $CrO_8{}^{3-}$, which is known to have the duodecahedral structure. The fact that $\langle g \rangle$ for these ions in the duodecahedral configuration is much different from that of the ions in solution is additional evidence that these ions do not possess the duodecahedral configuration in water solution.

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Notes

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Preparations and Properties of Chromium(II) Complexes. IV.[1] Complexes with Acetonitrile and Observations on Tetrahedral Chromium(II)

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Acetonitrile forms a variety of complexes with halides of first-row transition metals,[2] either by recrystallization of the halide from acetonitrile or by reaction of the metals with halogens (Cl_2, Br_2, I_2) in acetonitrile.[3-6] The majority of the chloride and bromide complexes of Mn(II), Fe(II), Co(II), Ni(II), and Zn(II) are of the type $MX_2{\cdot}2CH_3CN$. Apart from the Co(II) and Zn(II) complexes, they have octahedral structures with (presumably) bridging halides.[3-5] The iodides of Mn(II), Fe(II), Co(II), and Ni(II) form complexes of formula $MI_2{\cdot}3CH_3CN$ which have been shown[3-5] to contain octahedral and tetrahedral metal ions, as in

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$[M(CH_3CN)_6][MI_4]$. The reactions of Ti, V, and Cr metals with halogens in acetonitrile give, for the most part, simple octahedral addition compounds[3,6] of the type $MX_3 \cdot xCH_3CN$.[3,6]

The most stable complexes of copper(II) halides and acetonitrile appear[3] to be $CuX_2 \cdot CH_3CN$ (X = Cl, Br), although[7] $CuCl_2 \cdot 2CH_3CN$ and[8] $CuCl_2 \cdot {}^2/_3CH_3CN$ have been reported. The crystal structures[8] of $CuCl_2 \cdot xCH_3CN$ ($x = 1$ and $^2/_3$) show the presence of dimeric or polymeric units with halogen bridges and nitrogen-coordinated CH_3CN groups.

Continuing our studies[1] of $3d^4$ systems, chromium(II) halide complexes with acetonitrile have been prepared. It was thought that these complexes might be particularly interesting in view of the tetrahedral species formed with the iodides of Mn(II) through Ni(II).

Experimental Section

All preparations and measurements were carried out under inert atmospheric conditions as previously described.[9]

Dichlorobis(acetonitrile)chromium(II).—Chromium(II) chloride, anhydrous or hydrated,[9] is dissolved in the minimum quantity of hot ethanol, to which hot acetonitrile is added until a solid begins to crystallize. On cooling, pale blue crystals appear which are filtered off, washed with acetonitrile, and dried at room temperature under vacuum.

Anal. Calcd for $CrCl_2 \cdot 2CH_3CN$: C, 23.43; H, 2.95; Cr, 25.37; Cl, 34.59. Found: C, 23.2; H, 3.1; Cr, 25.4; Cl, 34.6.

Blue crystals, probably the complex contaminated with $ZnCl_2 \cdot 2CH_3CN$,[3] can be obtained by reducing a solution of chromium(III) bromide in acetonitrile[6] with Zn–Hg.

Dibromobis(acetonitrile)chromium(II).—Hexaaquochromium(II) bromide[9] is dehydrated by heating to 150° under high vacuum for 24 hr and transferred to a Soxhlet extraction thimble. The halide is extracted under nitrogen with dry acetonitrile (distilled from P_2O_5). Slowly, pale blue-green needles form in the extraction flask. The crystals, which are oxidized rapidly in the presence of oxygen when wet but more slowly when dry, are filtered off, washed with dry acetonitrile, and dried at room temperature under vacuum.

Anal. Calcd for $CrBr_2 \cdot 2CH_3CN$: Cr, 7.69; Br, 54.38. Found: Cr, 7.7; Br, 54.5.

Attempts to prepare $CrBr_2 \cdot 2CH_3CN$ by reducing a chromium(III) bromide acetonitrile solution[6] with Zn–Hg resulted in a mixture of blue and white (presumably[3] $ZnBr_2 \cdot 2CH_2CN$) crystals.

Diiodobis(acetonitrile)chromium(II).—A solution of chromium(III) iodide in acetonitrile[6] is reduced by Zn–Hg to give a bright blue solution.[3] The hot solution is filtered, and the pale blue crystals which separate on cooling are filtered off and dried under vacuum. The acetonitrile solution and the solid complex are oxidized immediately in the presence of trace amounts of oxygen.

Anal. Calcd for $CrI_2 \cdot 2CH_3CN$: C, 12.38; H, 1.56. Found: C, 12.5; H, 1.6.

Blue crystals, rapidly oxidized in air, are obtained by recrystallizing $CrI_2 \cdot 6H_2O$ from acetonitrile. They appear to have the approximate composition $CrI_2 \cdot 2CH_2CN \cdot 3H_2O$ and were not investigated further because of their extreme sensitivity to trace amounts of oxygen.

Anal. Calcd. for $CrI_2 \cdot 2CH_3CN \cdot 3H_2O$: C, 10.87; H, 2.74; Cr, 11.77; I, 57.42; N, 6.34. Found: C, 10.7; H, 2.6; Cr, 12.0; I, 59.5; N, 6.0.

Attempted Isolation of Tetrahalo Chromium(II) Complexes.—The addition of tetraalkylammonium chloride to acetonitrile and/or ethanol solutions of $CrCl_2 \cdot 2CH_3CN$ resulted in a solution from which only starting materials were recovered. With $CrBr_2 \cdot 2CH_3CN$, the addition of tetraalkylammonium bromide (in quantities we estimate to greatly exceed twice the molar quantity of $CrBr_2 \cdot 2CH_3CN$) produced a pale yellow solution, suggestive of the formation of a new species (*vide infra*). But here also only starting materials were obtained on evaporation or cooling. With $CrI_2 \cdot 2CH_3CN$, tetraalkylammonium (or arsonium) iodide addition produced some oxidation of the chromium(II).

Results

Dichlorobis(acetonitrile)chromium(II) is easily prepared in a pure state but decomposes in minutes in air.[10] The bromide complex appears to be more reactive than the chloride, while $CrI_2 \cdot 2CH_3CN$ is by far the most air-sensitive chromium(II) compound we have prepared[1,9,10] to date. As a result, it was very difficult to study. While small amounts of water generally do not interfere with the coordinating ability of acetonitrile, especially when the latter is in a large excess,[3] $CrBr_2 \cdot 2CH_3CN$ must be prepared under anhydrous conditions, otherwise complexes containing varying amounts of coordinated water are produced. Recrystallization of $CrI_2 \cdot 6H_2O$ from acetonitrile also gives a product containing both water and acetonitrile.

Infrared spectra in the 2300 cm^{-1} region show the acetonitrile to be coordinated through nitrogen as in other acetonitrile complexes.[3-6] The chloride and bromide complexes have room temperature moments of 4.81 BM ($\chi_g^{uncor} = 47.1 \times 10^{-6}$ cgs at 22°) and 4.85 BM ($\chi_g^{uncor} = 32.7 \times 10^{-6}$ cgs at 26°), respectively.

The principal visible and near-infrared absorption spectra maxima for each of the complexes, with their solution molar extinctions, are recorded in Table I. Reflectance spectra of the chloride and bromide complexes are quite similar, both in the shape and position of the bands. In both complexes, the low-energy shoulder is clearly resolved into a maximum at low temperatures. These spectra are very similar to the spectra of $CrCl_2 \cdot 2py$ and $CrBr_2 \cdot 2py$, which have absorption maxima at 15,050 and 10,800 cm^{-1} and at 14,300 and 10,300 cm^{-1}, respectively.[10] The reflectance spectrum of $CrI_2 \cdot 2CH_3CN$, however, is significantly different from the spectra of the chloride and bromide. At both room and low temperatures the low-energy band appears as a broad maximum, in almost the same position as in the chloride and bromide, while the second band is shifted 3000 cm^{-1} to higher energies.

X-Ray powder patterns of $CrCl_2 \cdot 2CH_3CN$ and $CrBr_2 \cdot 2CH_3CN$ show that the two complexes are not isomorphous. Neither pattern resembles those of the two isomorphous, polymeric[10] $CrX_2 \cdot 2py$ complexes.

Solution spectra maxima of the complexes in acetonitrile with and without added halide ions are also recorded in Table I. $CrCl_2 \cdot 2CH_3CN$ is only sparingly soluble in acetonitrile, but a spectrum was obtained with a saturated solution in 10-cm cells. The band maximum appears in almost the same position as in the reflectance spectrum; however, the band in the 10,000 cm^{-1} region is seen only as a slight asymmetry on the low-energy side of the main band. The solution spectrum of

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TABLE I

ABSORPTION MAXIMA (cm^{-1}) OF $CrX_2 \cdot 2CH_3CN$ COMPLEXES

			With tetraalkylammonium halide[d]	
$CrCl_2 \cdot 2CH_3CN$				
Reflectance	13,300[b]	9,800 sh[b]		
	13,900[c]	9,900[c]		
0.0016 *M* CH_3CN	13,200 (35)[a]	~10,000 sh	13,200 sh	10,100 (~50)
0.0282 *M* C_2H_5OH	12,500 (34)	~10,400 sh		11,600 (~40)
$CrBr_2 \cdot 2CH_3CN$				
Reflectance	13,200[b]	9,600 sh[b]		
	13,700[c]	9,300[c]		
0.0045 *M* CH_3CN	11,800 (~80)	~10,000 sh		10,000 (~230)
$CrI_2 \cdot 2CH_3CN$				
Reflectance	16,200[b]	10,000[b]		
	16,700[c]	10,400[c]		
0.279 *M* CH_3CN	15,400 (3.6)	10,000 (~1)		

[a] Molar extinction coefficients, when available, are given in parentheses; sh, shoulder. [b] Room temperature. [c] Liquid nitrogen temperature. [d] Excess estimated to be much greater than twice the concentration of CrX_2. Additional halide produces no further changes.

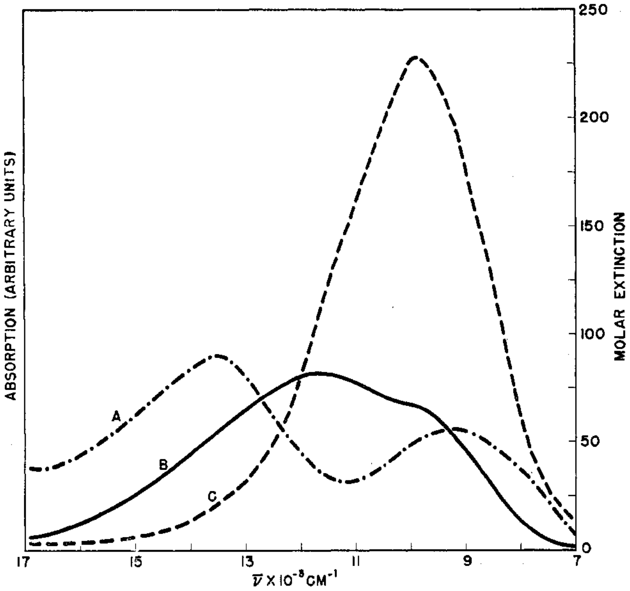

Figure 1.—Spectra of $CrBr_2 \cdot 2CH_3CN$: A, reflectance, 77°K; B, 0.0045 *M* in CH_3CN solution; C, solution B plus large excess of $(C_2H_5)_4NBr$.

$CrBr_2 \cdot 2CH_3CN$ in acetonitrile differs considerably from the reflectance spectrum (see Figure 1).

When excess tetraalkylammonium halide is added to the solvent, pronounced effects on the spectra of the complexes are observed. With $CrCl_2 \cdot 2CH_3CN$ in acetonitrile containing $(C_2H_5)_4NCl$, the solubility increases and the absorption maximum shifts to ~10,100 cm^{-1} (ϵ ~50). However, a shoulder remains at the same position as the band maximum before halide addition. Similar but less pronounced shifts are observed in ethanol. With $CrBr_2 \cdot 2CH_3CN$, addition of halide (see Figure 1) shifts the band from the visible nearly completely into the infrared. The color of the solution changes accordingly from blue-green to pale yellow. A significant increase in the molar extinction also is observed. Addition of halide ions to the iodide solution in acetonitrile gives some oxidation. Although no accurate measurements could be obtained, the 15,400 cm^{-1} band appears to move to lower energies with an increase in extinction coefficient.

Discussion

A general discussion of the spectra of $3d^4$ systems has been presented previously.[9] Since the reflectance spectra of $CrCl_2 \cdot 2CH_3CN$ and $CrBr_2 \cdot 2CH_3CN$ are very similar to the spectra[10] of $CrX_2 \cdot 2py$ (X = Cl, Br), similar assignments of the bands are suggested. If the low-energy band is the transition between the split components of the ^5E_g ground state, as is thought to be the case in the hydrates,[9] then the higher energy band, which contains the transitions to the split $^5T_{2g}$ state, includes the transition with an energy corresponding to $10Dq$. The shift to higher energy in the pyridine complex is consistent with the slightly higher position of pyridine relative to acetonitrile in the spectrochemical series.[3] Based on spectral evidence, the environment of the chromium(II) in $CrX_2 \cdot 2CH_3CN$ (X = Cl, Br) appears to be similar to that in $CrX_2 \cdot 2py$ (X = Cl, Br), *i.e.*, distorted octahedral with four halides and two CH_3CN groups surrounding the chromium(II). The X-ray powder patterns of $CrX_2 \cdot 2CH_3CN$ (X = Cl, Br) contribute little additional information to the structural problem except to indicate that some differences between the structures of the chloride and bromide must exist.

The position of the main band in the reflectance spectrum of $CrI_2 \cdot 2CH_3CN$ at ~3000 cm^{-1} higher energy than the band in chloride and bromide complexes suggests a major structural change occurs with the iodide. The molar extinction coefficients at the band maxima in acetonitrile solution (Table I) also are significantly different. The low values observed (ϵ ~1–4) are consistent with the presence of an essentially centrosymmetric structure in solution. These molar extinctions are similar to those for Cr^{2+}(aq) where a molar extinction of 5.0 was obtained[9] for the principal band. The reflectance and solution spectra of $CrI_2 \cdot 2CH_3CN$ suggest that site symmetry of the chromium(II) is similar in the solid state and in solution. This suggests the absence of large quantities of $Cr(CH_3CN)_6^{2+}$ ions in solution.

The chromium(II) halide–acetonitrile complexes were studied in the presence of excess tetraalkylammonium (or arsonium) halides in the hope of isolating solid tetrahedral chromium(II) compounds. Gruen and McBeth[11] presented spectral evidence for such a tetrahedral species from the spectrum of $CrCl_2$ in a KCl–LiCl eutectic. They assigned a band at 9800 cm^{-1} ($\epsilon \sim 45$) to the $^5E \leftarrow {}^5T_2$ absorption in T_d symmetry. Other bivalent first-row transition metal ions give typical tetrahedral spectra in this melt. In a CdS(s) crystal, the spectrum[12] and paramagnetic resonance[13] have suggested that the chromium(II) occupies a slightly distorted tetrahedral site. A spectral band near 5500 cm^{-1} is reported.[12] Thus a 4300 cm^{-1} separation exists between what presumably is the $^5E \leftarrow {}^5T_2(T_d)$ absorption of chromium(II) in the two media studied. This apparent discrepancy could be due to the presence of a *distorted* tetrahedral arrangement (compare with the data on $CuCl_4^{2-}$ in ref 1) about the chromium(II) in the eutectic.

The spectrum[14] of $CrCl_2$ in anhydrous $AlCl_3$(l), where octahedral holes exist, shows a band slightly different in position from the band in the eutectic. Unfortunately, intensities could not be measured.[14] Anhydrous $CrCl_2$, which contains six-coordinate[15] chromium(II), also shows a band[9] at nearly the same frequency. The reflectance spectrum suggests the intensity ($\epsilon \sim 1$–10) of this band is not significantly different from that[9] of other six-coordinate chromium(II) complexes, however.

Unlike copper(II) chloride,[16] there is no evidence for MCl_4^{2-} formation in acetonitrile or ethanol on addition of excess chloride.

With $CrBr_2 \cdot 2CH_3CN$, however, spectral changes consistent with solvolysis[17] occur in acetonitrile (Figure 1). Addition of bromide causes a shift of the principal visible absorption to lower energy and a fourfold increase in the extinction coefficient. Qualitatively similar changes occur when tetrahedral MX_4^{2-} complexes of the other bivalent transition metals are formed[18] in this solvent.[3]

While the extinction coefficient rules out the formation of a centrosymmetric six-coordinate $CrBr_6^{4-}$ ion, the absorption appears at rather higher energies than predicted for a regular tetrahedral species and, in fact, appears near the energy of the $CrCl_4^{2-}$ band in the KCl–LiCl eutectic.[11] Thus one reasonably concludes that a distorted tetrahedral anion predominates in the solution.

As indicated previously, all attempts to isolate a tetrahedral CrX_4^{2-} complex failed. Unfavorable radius ratios[19] may be responsible in part for this since chromium(II) is the largest bivalent, first-row transition metal ion which gives any evidence at all for tetrahedral anion formation. We are currently attempting to correct these unfavorable size effects by preparing complexes of the type L_2CrX_2, where L is sterically large.

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[16] A further difference between copper(II) and chromium(II) is obvious from the acetonitrile complexes themselves. The chromium(II) halides form complexes with two CH_3CN molecules while copper(II) chloride and bromide form mono(acetonitrile) complexes. Attempts to prepare[7] $CuCl_2 \cdot 2CH_3CN$ were not successful.

[17] Solvolysis of some transition metal halides in nonaqueous solvents has been discussed previously. For example, the articles by S. Buffagni and T. M. Dunn, *J. Chem. Soc.*, 5105 (1961), and D. A. Fine, *J. Am. Chem. Soc.*, **84**, 1139 (1962), consider the various complexes formed with cobalt(II) halides in a number of solvents, *i.e.*, $[MX_4]^{2-}$, $[MX_3S]^-$, $[MX_2S_2]$, etc., where X = Cl, Br, I and S = solvent. Equilibria, leading to the formation of similar complexes, are thought to exist in the $CrBr_2$–CH_3CN solution.

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Polarographic Investigation of the Allyl Alcohol Complex of Copper(I) in Aqueous Solution

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An investigation of the solubility of cuprous chloride in aqueous solutions of allyl alcohol has shown that copper(I) ion forms a 1:1 complex with allyl alcohol.[1] A stability constant of $10^{4.7}$ was determined for the species Cu(alc)$^+$. The investigation was complicated, however, by the formation of the chloride complexes $CuCl_2^-$ and Cu(alc)Cl.

Using polarography we have determined the formation constant of the allyl alcohol complex of copper(I) in aqueous media 0.1 *M* in $NaClO_4$. The concentration of allyl alcohol ranged from 1.00×10^{-2} to 1.00 *M*. Half-wave potential values were obtained for both the Cu(I),Cu(Hg) couple and the Cu(II),Cu(I) couple at both the dropping mercury electrode and the dropping copper amalgam electrode. In the former case copper(II) was added to the solution as the perchlorate and in the latter case copper was not present in solution. The values of $E_{3/4} - E_{1/4}$ for all the polarographic waves fell within the range of 0.056–0.060 v, indicating reversibility of the electrode reactions.[2] The half-wave potentials measured at the mercury electrode were in close agreement with the half-wave potentials obtained at the amalgam electrode.

The polarographic reduction of Cu^{2+} to Cu(Hg) at the dropping mercury electrode (or oxidation of Cu(Hg) to Cu^{2+} at the dropping copper amalgam electrode) in aqueous noncomplexing media proceeds *via* a one-step, two-electron process. The addition of

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