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Properties of Chromium(II) Complexes. I. Electronic Spectra of the Simple Salt Hydrates[1]

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The electronic absorption spectra of the chloride, bromide, iodide, sulfate, and perchlorate hydrates and the anhydrous chloride and fluoride of chromium(II) have been investigated by diffuse reflectance at room temperature and 77°K. Solution spectra of the hydrates also have been observed. Besides the principal d–d transition occurring in the visible region of the spectrum, another LaPorte-forbidden band is found near 10,000 cm.$^{-1}$. Resolution of the $^5T_{2g} \leftarrow {}^5E_g$ (in O_h) absorption band in the 6000–20,000 cm.$^{-1}$ region into several components is discussed in terms of extensive distortion of these high-spin complexes from octahedral symmetry.

Introduction

Studies in this laboratory have been directed toward the examination of the physical and chemical properties of complexes in which the metal has a [core]$3d^4$ electron configuration. Particular emphasis to date[2,3] has been placed on the high-spin complexes of chromium(II) and manganese(III). Since relatively little is known about the properties of complexes with these ions, an effort is being made to consider the influence various types of ligands chosen in a systematic manner have on the chemical and physical properties of the complexes formed.

Measurement of the physical properties of chromium(II) complexes is plagued by the ease with which the chromium(II) is oxidized by air. Until the recent rediscovery by Lux and his co-workers[4,5] that electrolytic chromium is oxidized to chromium(II) by dilute aqueous acids[6a]—not to chromium(III) as happens with less pure metal—chromium(II) complexes generally were made either by reduction of chromium(III) complexes with zinc metal or by electrolytic methods.[6b] The former procedure often contaminates the product with zinc(II) and the latter is very time consuming. With electrolytic chromium, it is possible to prepare aqueous solutions of chromium(II) salts conveniently. From these solutions pure complexes may be crystallized.

In this paper the solution spectra, room temperature magnetic susceptibilities, and diffuse reflectance spectra at room temperature and 77°K. of some hydrated salts of chromium(II) are presented and discussed. The hydrated salts studied are $CrCl_2 \cdot 4H_2O$, $CrSO_4 \cdot 5H_2O$, and $CrX_2 \cdot 6H_2O$, where X = Br^-, I^-, or ClO_4^-. Few papers have reported the spectrum[7–9] of aqueous chromium(II) and no previous study to our knowledge has included the 5000–10,000 cm.$^{-1}$ region of the spectrum where a low-energy electronic band is found.[10,11] The diffuse reflectance spectra of anhydrous $CrCl_2$ and CrF_2 also are included in this work.

Experimental

Preparations.—The chloride, bromide, iodide, and sulfate[12] hydrates of chromium(II) were prepared by allowing electrolytic chromium metal (obtained from Schmeltztechnik G.m.b.H., München 42, Germany, through United Mineral and Chemical Corp., New York, N. Y.) to react with the corresponding acids, as previously described.[4] All the compounds are stable indefinitely when stored under nitrogen.

Analyses and magnetic moments (measured by the Standard Gouy method[14]) are recorded in Table I.

TABLE I

Compound	Cr analyses[a] Found	Cr analyses[a] Calcd.	Magnetic properties[b] χ_g (293°K.)	Magnetic properties[b] μ_{eff} (cor.), B.M.
$CrCl_2 \cdot 4H_2O$	26.5	26.68	52.0×10^{-6}	4.94 ± 0.05
$CrBr_2 \cdot 6H_2O$	16.1	16.26	31.2×10^{-6}	4.90 ± 0.05
$CrI_2 \cdot 6H_2O$	12.5	12.57	25.0×10^{-6}	4.98 ± 0.05
$CrSO_4 \cdot 5H_2O$	21.7	21.85	42.5×10^{-6}	4.92 ± 0.05
$Cr(ClO_4)_2 \cdot 6H_2O$	14.4	14.49	...	...

[a] Cr estimated by oxidizing sample to Cr(VI) with $(NH_4)_2S_2O_8$–$AgNO_3$, adding an excess of standard Fe(II), and back titrating with standard dichromate (see A. I. Vogel, "Quantitative Inorganic Analysis," Longmans, London, 1955, p. 297). [b] Average χ_g at different field strengths and different tube packings. Diamagnetic corrections obtained from Figgis and Lewis[14] and P. W. Selwood, "Magnetochemistry," Interscience Publishers, New York, N. Y., 1956, p. 78.

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(1) Some of this work was reported at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

(2) J. P. Fackler, Jr., I. D. Chawla, and D. G. Holah, "Proceedings of the Eighth International Conference on Coordination Chemistry," V. Gutmann, Ed., Springer-Verlag, New York and Vienna, 1964, p. 75.

(3) (a) J. P. Fackler, Jr., and I. D. Chawla, *Inorg. Chem.*, **3**, 1130 (1964); (b) J. P. Fackler, Jr., T. S. Davis, and I. D. Chawla, *ibid.*, **4**, 130 (1965).

(4) H. Lux and G. Illman, *Chem. Ber.*, **91**, 2143 (1958).

(5) H. Lux, L. Eberle, and D. Sarre, *ibid.*, **97**, 503 (1964).

(6) (a) R. L. Pecsok and J. Bjerrum, *Acta Chem. Scand.*, **11**, 1418 (1957); (b) R. L. Pecsok and W. P. Schaeffer, *J. Am. Chem. Soc.*, **83**, 62 (1961).

(7) O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).

(8) H. L. Schläfer and H. Skoludek, *Z. physik. Chem.* (Frankfurt), **11**, 277 (1957).

(9) T. Dreisch and O. Kallschenen, *Z. physik. Chem.* (Leipzig), **B45**, 19 (1939).

(10) W. A. Runciman and R. W. G. Syme, *Phil. Mag.*, **8**, 605 (1963), suggest the presence of a low-energy band in crystalline $CrCl_2 \cdot 4H_2O$.

(11) R. J. H. Clark, *J. Chem. Soc.*, 417 (1964), observes a similar low-energy band in anhydrous CrF_2(s) at 11,400 cm.$^{-1}$.

(12) Hydrated sulfates of chromium(II) have been reported at various times to contain one,[5] five,[4] six,[13] and seven[10] water molecules (see also F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York, N. Y., 1962, p. 683; N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford, England, 1952, p. 1025). Lux attempted to prepare $CrSO_4 \cdot 7H_2O$ but found only $CrSO_4 \cdot 5H_2O$[4] and $CrSO_4 \cdot H_2O$[5] by dehydration of the five-hydrate. Presumably Runciman and Syme,[10] who did not report chemical analysis, studied $CrSO_4 \cdot 5H_2O$.

(13) E. Lips, *Helv. Phys. Acta*, **7**, 537 (1934); *Chem. Abstr.*, **28**, 7089[1] (1934).

(14) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1961, p. 409.

Reactions and filtrations are carried out in closed ground-glass equipment[15] inside a nitrogen-filled box which is shown schematically in Figure 1. Lamp grade (General Electric) nitrogen is continually cycled through a purification train while the gas pressure in the box is maintained at approximately 2 in. of water above atmospheric; a thermistor switches off the pump should the pressure fall below atmospheric.

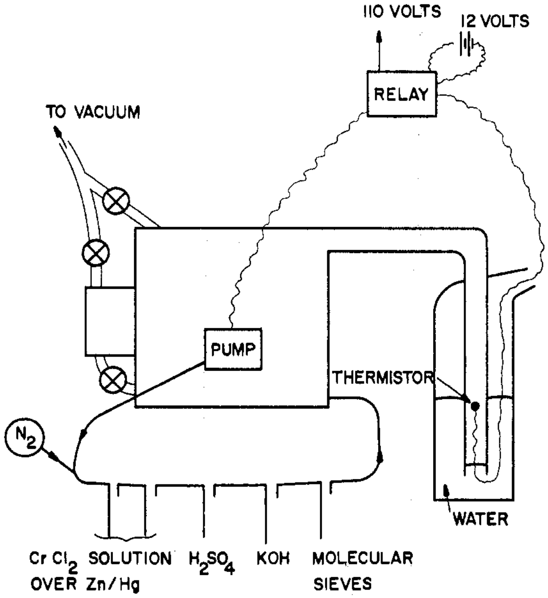

Figure 1.—Drybox assembly.

Chromium(II) Perchlorate.—Chromium metal (4 g.) reacts (after activation by dipping in dilute HCl until a reaction starts, then washing) with 40 ml. of 20% perchloric acid to give a deep blue solution from which blue crystals are obtained on cooling and evaporation. These crystals, which have been isolated previously,[4] but not analyzed, decompose in a few hours even when stored under nitrogen.

Spectral Studies.—Solution spectra were measured in matched 1-cm. silica cells on a Cary Model 14 spectrophotometer. Reflectance spectra were observed with a Beckman DK-2 spectrophotometer fitted with a standard reflectance attachment. The circular glass dewar used for low-temperature spectra is shown in cross section in Figure 2. The silvered inner glass surfaces and the cylinders of silver foil greatly reduce the loss of light by reflections inside the walls of the dewar after reflecting from the sample. The small gap between the silver foil cylinders eliminates heat conduction. Silicone high vacuum grease is used between the dewar and the two silica plates, which are drawn tightly against the dewar when the latter is evacuated. At liquid nitrogen temperatures, a nitrogen gas jet is directed at the front plate to eliminate condensation.

Results

The spectra presented in Table II indicate clearly that each of the salts studied forms the same aqueous chromium(II) species in water. The similarity of the spectra of solid $CrX_2·6H_2O$, where X = Br^-, I^-, or ClO_4^-, and those of the aqueous solutions suggests that the chromium(II) species is the same in each phase. Presumably the aqueous species formed is $Cr(H_2O)_6.^{2+}$ Similar ions apparently exist in the solid compounds,[16] especially in $Cr(ClO_4)_2·6H_2O$.

Powder X-ray data show $CrBr_2·6H_2O$ is not isomorphous with $NiCl_2·6H_2O$ or $CoCl_2·6H_2O$. These latter

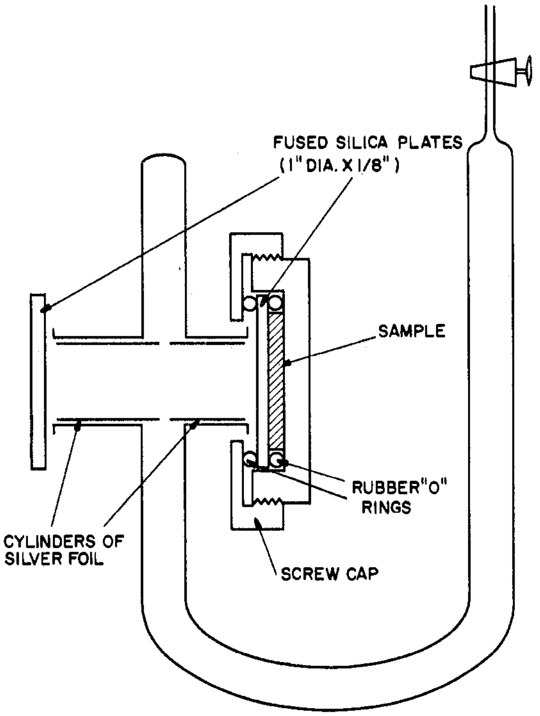

Figure 2.—Glass dewar and sample holder for low-temperature reflectance spectra.

TABLE II

SPECTRA OF CHROMIUM (II) COMPLEXES

Compound	Phase[a]	Frequency × 10^{-3} cm.$^{-1}$
CrF_2[b]	Solid	11.5, 14.7
$CrCl_2$[c]	Solid	8.35 (sh),[d] 11.6, 16.1 (w),[e] 17.4 (w),[e] 19.0 (w)[e]
	Solid (77°K.)	8.75, 12.0, 16.3 (w),[e] 17.5 (w),[e] 19.0 (w)[e]
$CrCl_2·4H_2O$	Solid	10.0 (sh), 14.7
	Solid (77°K.)	10.0, 13.1 (sh), 16.0, 18.9 (sh)
	Single crystal[10] (77°K.)	. . ., 13.1, 15.2, 18.8
	Solution (0.105 *M*)	9.5 (sh, 2.0), 14.0 (5.1)
$CrBr_2·6H_2O$	Solid	10.5, 14.9
	Solid (77°K.)	10.5 (vb), 15.7, 18.2 (sh)
	Solution (0.100 *M*)	9.5 (sh, 1.9), 14.0 (5.0)
$CrI_2·6H_2O$	Solid	Broad band, max. ~ 14.3 skew on low-energy side
	Solid (77°K.)	
	Solution (0.139 *M*)	9.5 (sh, 2.0), 14.0 (4.8)
$CrSO_4·5H_2O$	Solid	10.3 (sh), 14.3
	Solid (77°K.)	10.25, 13.7 (sh), 15.25, 18.9 (sh)
	Solution (0.170 *M*)	9.5 (sh, 2.0), 14.0 (5.2)
$Cr(ClO_4)_2·6H_2O$	Solid	10.0 (sh), 14.1
	Solid (77°K.)	10.0, 15.4 (b), 18.9 (sh)
	Solution (0.195 *M*)	9.5 (sh, 1.8), 14.0 (5.0)

[a] Diffuse reflectance of solids, transmission of liquids, at room temperature unless otherwise stated. With the exception of $CrI_2·6H_2O$, the frequencies are thought to be accurate to ±100 cm.$^{-1}$. For $CrI_2·6H_2O$ this accuracy is reduced due to the difficulty of obtaining a homogeneous powdered sample. [b] Clark[11] reports bands at 11,400 and 14,700 cm.$^{-1}$. A band reported at 23,000 cm.$^{-1}$ was not found [c] The spectrum reported by Clark[11] shows considerable amounts of chromium(III). [d] Apparent intensity or molar absorbance in parentheses; sh, shoulder; w, weak; vb, broad. [e] Probably spin-forbidden bands of chromium(II).

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(15) (a) D. G. Holah, Ph.D. Thesis, University of Hull, 1963; (b) D. G. Holah, *J. Chem. Educ.*, in press.

(16) It should be stated that no strongly compelling evidence exists which proves all six water molecules in each of the $CrX_2·6H_2O$ species studied are bonded to the metal. The spectral data are not conclusive on this point since the differences observed may be due either to second-order effects caused by the various anions or to different arrangements of the ligands coordinated to the metal. Since both ligand field bands, not just one as might be expected for a *trans* halide arrangement using a simple crystal-field model, appear at slightly higher energies in the halides than in $Cr(ClO_4)_2·6H_2O$, it would appear that the halides are not bonded to the metal; halide bonding would tend to reduce the average effective ligand field. Of course, tetragonal splitting may be producing a ligand field not describable even qualitatively by averaging the effects of the different ligands.

compounds have a *trans* octahedral[17] $MCl_2(H_2O)_4$ arrangement. The chromium(II) complex also is not isomorphous with $CoBr_2 \cdot 6H_2O$, which is reported to have an analogous structural arrangement[18] in the neighborhood of the cobalt(II) ion.

The chromium(II) solutions observed in this study contained a concentration of chromium(III) of less than 0.003 *M* as estimated from the appearance of a band at 24,400 cm.$^{-1}$, molar absorbance ~15 l. mole^{-1} cm.$^{-1}$. The presence (or absence) of this band is an excellent indication[6b] of the quantity of chromium(III) in the system.[8] A further band[19] of a chromium(III) species grows as a shoulder on the main chromium(II) absorption in the region of 17,400 cm.$^{-1}$, although extensive oxidation of the chromium(II) solution must occur before this latter band becomes visible because of its position near the principal chromium(II) band.

The presence of a band near 10,000 cm.$^{-1}$ in each of the chromium(II) complexes studied is to be noted. This band has been observed previously only in the solution spectrum of $CrI_2 \cdot 2CH_3CN$[15a] and in the reflectance spectrum of CrF_2.[11] The shoulder which appears in the solution spectra of the aqueous chromium(II) species (Figure 3) becomes a readily discernible band in diffuse reflectance, especially at 77°K. (Figure 4).

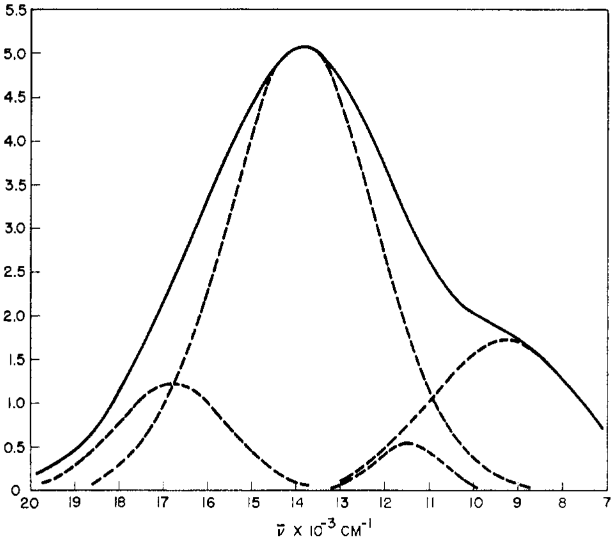

Figure 3.—Spectrum of $Cr(H_2O)_6^{2+}$ and the Gaussian analysis.

The molar absorbances found at the band maxima for solutions are characteristic of LaPorte-forbidden spin-allowed transitions in transition metal complexes.[20] The broad nature of the principal band (width at half-height ~6000 cm.$^{-1}$) gives it an integrated intensity of ~1.3×10^{-4}.

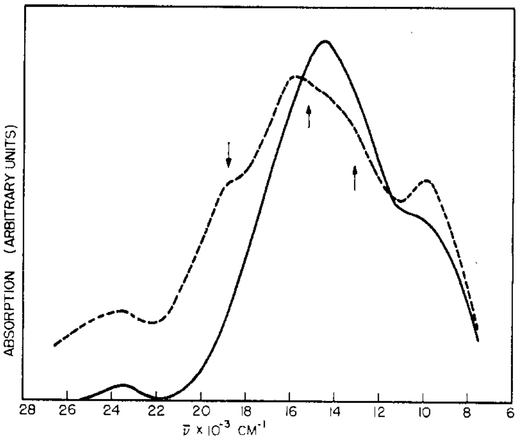

Figure 4.—Reflectance spectra of $CrCl_2 \cdot 4H_2O$: ———, room temperature; - - - -, liquid nitrogen temperature. Arrows denote the positions of the bands found in the polarized single crystal spectrum by Runciman and Syme.[10]

Runciman and Syme[10] published the single crystal polarized absorption spectrum of $CrCl_2 \cdot 4H_2O$ from 25,000 to 10,000 cm.$^{-1}$, observed at room temperature and at 78°K. Their work shows the presence of three d–d bands within the region studied. These authors indicate a fourth band may be present below 10,000 cm.$^{-1}$; however, it was not observed due to the lack of proper equipment. The diffuse reflectance spectrum (Figure 4) of $CrCl_2 \cdot 4H_2O$ clearly shows the presence of a band at 10,000 cm.$^{-1}$. At 77°K. this band is well resolved from the main absorbance. Bands also appear to be centered near 18,900, 16,000, and 13,100 cm.$^{-1}$. As mentioned earlier, a low-energy band is found in the spectrum of each of the complexes studied as well as in the spectra[21] of chromium(II) halide–acetonitrile complexes.

It is particularly difficult in reflectance measurements on these systems to eliminate the chromium(III) absorption in the 25,000 cm.$^{-1}$ region. This is because the light reflection is from the *surface* of a ground or crystalline chromium(II) material, which is precisely where traces of oxidation may occur. It was thought that when this band is present, the shoulder at about 18,800 cm.$^{-1}$ observed at low temperatures may be the second chromium(III) absorption. However, spectra of the chloride have been obtained where the 25,000 cm.$^{-1}$ region is virtually clear but with the 18,800 cm.$^{-1}$ absorption still quite clearly visible.

The room temperature magnetic susceptibilities of the chromium(II) complexes reported in this work show the presence of four unpaired electrons per chromium(II). Since the moments observed (Table I) are very close to the "spin only" value of 4.9 B.M., a lack of significant orbital contribution is apparent. The moments observed for $CrCl_2 \cdot 4H_2O$ and $CrSO_4 \cdot 5H_2O$ agree with reported values.[13,22]

Discussion

The observation in this work of a new band near or below 10,000 cm.$^{-1}$ for all the simple chromium(II)

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[17] J. Mizuno, *J. Phys. Soc. Japan*, **16**, 1574 (1961).

[18] E. V. Stroganov, S. N. Andrew, I. I. Kochina, and V. E. Solov'ov, *Vestn. Leningr. Univ.*, **16**, *Ser. Fiz. i Khim.*, **3**, 114 (1961); *Chem. Abstr.*, **56**, 4184*e* (1962).

[19] The 24,400 cm.$^{-1}$ band presumably is the $^4T_{1g}(F) \leftarrow {}^4A_{2g}(F)$ transition (in O_h symmetry) for a chromium(III) species. The band appearing near 17,400 cm.$^{-1}$ can be assigned[20] to the $^4T_{2g}(F) \leftarrow {}^4A_{2g}(F)$ transition.

[20] T. M. Dunn, "Modern Coordination Chemistry," J. Lewis and R. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p. 277 ff.

[21] D. G. Holah and J. P. Fackler, Jr., to be published.

[22] A. Earnshaw, L. F. Larkworth, and K. S. Patel, *Proc. Chem. Soc.*, 281 (1963).

species studied clearly shows that these complexes are strongly distorted (see below) from octahedral symmetry. An octahedral complex of this high-spin 3d^4 ion would be expected to show only a single spin-allowed d–d transition, $^5T_{2g} \leftarrow {}^5E_g$, in the visible region of the spectrum. The fact that at least two such bands are observed in each of the complexes indicates they all have a molecular symmetry of D_{4h} or lower (Figure 5), depending on the particular complex studied. The observation of the low-energy band in $CrCl_2 \cdot 4H_2O$ suggests that all four spin-allowed d–d bands for this C_{2h} symmetry molecule[10] now have been observed. Single crystal polarized spectral studies to energies less than 10,000 cm.$^{-1}$ still must be conducted to confirm this point, however, since the diffuse reflectance measurements, even at 77°K., do not unequivocally show the presence of all three bands observed by Runciman and Syme.[10] The width of the band system centered at 16,000 cm.$^{-1}$ is consistent with this interpretation, however. The distinctly different[10] Cr–O distances of 2.07 and 2.80 Å. along with a Cr–Cl distance of 2.42 Å. suggest that it is reasonable to expect the significant splittings observed.

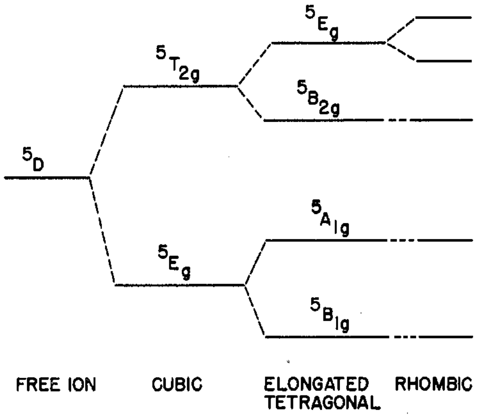

Figure 5.—Splitting of the ^5D spectroscopic term under cubic, elongated tetragonal, and rhombic fields.

Examination of a Tanabe–Sugano splitting diagram for a 3d^4 ion in an octahedral field[17] suggests the $^3T_{1g} \leftarrow {}^5E_g$ transition should appear near 12,000 cm.$^{-1}$ for a complex with Δ ($\equiv 10Dq$) $\sim$ 13,000 cm.$^{-1}$. The band centered near 9500 cm.$^{-1}$ might be considered to be this transition; however, two things run counter to such an assignment. The integrated intensity of $\sim 3 \times 10^{-5}$ l. mole^{-1} cm.$^{-2}$ for the low-energy band in Cr^{2+}(aq) is approximately one-fifth of the total integrated intensity of the band system centered near 15,000 cm.$^{-1}$. This is considerably larger than the intensity expected if the transition were spin-forbidden. Also, the energy of the $\sim$9500 cm.$^{-1}$ band appears to increase with increasing ligand field strength of the ligands (Table II and ref. 21). This is contrary to what is expected for a $^3T_{1g} \leftarrow {}^5E_g$ transition. However, it is recognized that this argument is complicated by the apparent distortion of the complexes studied from a regular octahedral configuration. Spin–orbit coupling, which could increase the intensity of spin-forbidden transitions, is thought to be small in 3d^4 ions.[14]

Orgel[23] and others[24] attributed the broad, highly asymmetric visible band in aqueous chromium(II) spectra to be a tetragonal distortion of octahedral $Cr(H_2O)_6^{2+}$, brought about because of the Jahn–Teller effect.[25-30] Such tetragonal distortions (axial elongation) have been observed in chromium(II) compounds studied crystallographically.[31,32] The presence of the low-energy band is expected if the molecules are substantially distorted from an octahedral configuration.[10,27,28]

Assuming an axially elongated octahedral configuration exists for $Cr(H_2O)_6^{2+}$ in solution, the energy level diagram of Figure 5 is obtained. Theoretical studies[27,28] suggest a separation of 2300 cm.$^{-1}$ for the ^5E_g and $^5B_{2g}$ levels. The principal band in the aqueous solutions observed here and in the reflectance spectra of the $Cr(ClO_4)_2 \cdot 6H_2O$, $CrSO_4 \cdot 5H_2O$, $CrBr_2 \cdot 6H_2O$, and $CrI_2 \cdot 6H_2O$ species certainly is of sufficient width to contain two bands separated by $\sim$2000 cm.$^{-1}$. Assuming this treatment is qualitatively correct, the electronic band at $\sim$10,000 cm.$^{-1}$ is assigned to the $^5A_{1g} \leftarrow {}^5B_{1g}$ transition.[33] The $^5E_g \leftarrow {}^5B_{1g}$ transition presumably centers near 15,000–16,000 cm.$^{-1}$, while the $^5B_{2g} \leftarrow {}^5B_{1g}$ transition is not resolved (except possibly in the sulfate), although there is asymmetry on the low-energy side of the major band, which appears in the same region. In the four complexes mentioned above, the reflectance spectra all show slight evidence for chromium(III) in the 25,000 cm.$^{-1}$ region, so that the 18,900 cm.$^{-1}$ shoulder, which is very much weaker than in the chloride and not seen by transmission in solutions, cannot be conclusively assigned to chromium(II). If it is due to chromium(II), as Runciman and Syme[10] indicate for the sulfate, the possibility that the molecular symmetry of the complexes studied may be lower than D_{4h} must be considered. The site symmetry for chromium(II) in $CrSO_4 \cdot 5H_2O$, which is isomorphous[5,34] with $CuSO_4 \cdot 5H_2O$, is not strictly D_{4h} in the crystal, hence the effective symmetry may be low enough to remove all orbital degeneracies. The distortion may be even more pronounced at liquid nitrogen temperatures.

The less well-defined splitting of the d–d band in the

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(23) L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).

(24) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **3**, 304 (1958).

(25) H. Hartman, H. L. Schläfer, and K. H. Hansen, *Z. anorg. allgem. Chem.*, **289**, 40 (1957).

(26) H. A. Jahn and E. Teller, *Proc. Roy. Soc.* (London), **A161**, 220 (1937).

(27) I. B. Bersuker, *Zh. Strukt. Khim.*, **2**, 350 (1961); *Chem. Abstr.*, **56**, 9534*f* (1962).

(28) I. B. Bersuker, *Opt. Spektroskopiya*, **11**, 319 (1961); *Zh. Strukt. Khim.*, **3**, 64 (1962); *Chem. Abstr.*, **58**, 10878*a* (1963).

(29) N. S. Ham, *Spectrochim. Acta*, **18**, 775 (1962).

(30) A. D. Liehr, *Progr. Inorg. Chem.*, **3**, 218 (1962).

(31) J. W. Tracey, N. W. Gregory, and E. C. Lingafelter; J. D. Dunitz and H. C. Mey; R. E. Rundle and C. Scheringer; H. I. Yokel and M. K. Wilkeman, *Acta Cryst.*, **14**, 927 (1961).

(32) J. W. Tracy, N. W. Gregory, J. M. Stewart, and E. C. Lingafelter, *ibid.*, **15**, 460 (1962).

(33) The observed splitting of the ^5E_g (in O_h) ground state according to this assignment is somewhat larger than the splitting calculated by Liehr and Ballhausen.[24] These authors suggested a splitting of 6517 cm.$^{-1}$. There is no evidence for another electronic band between 4000 and 9000 cm.$^{-1}$.

(34) G. E. Bacon and N. A. Curry, *Proc. Roy. Soc.* (London), **A266**, 95 (1962).

spectrum of Cr^{2+}(aq) as compared with room temperature and low temperature reflectance spectra of the solid is expected if minima exchange[30] (Bersuker[27,28] calls this "restricted motion") occurs between the three equilibrium configurations[35] corresponding to tetragonal distortions of the octahedral complex. Incorporating the $Cr(H_2O)_6^{2+}$ complex in a crystalline lattice increases the barrier tending to prevent minima exchange from occurring.[30] Lowering the temperature of the solid further reduces the vibrational energy available to produce this exchange.

The choice of an axially *elongated* octahedron for the structure of $Cr(H_2O)_6^{2+}$ may appear somewhat arbitrary since an axially compressed octahedron equally well satisfies the Jahn–Teller theory. However, chromium(II) complexes tend to be isomorphous with the analogous copper(II) complexes, as for example in the following chromium(II) and copper(II) compounds[5]: $MSO_4 \cdot 5H_2O$, $M(NH_3)_4SO_4 \cdot H_2O$, $MCl_2 \cdot 2py$, $M(CH_3CO_2)_2 \cdot H_2O$. Since most copper(II) compounds have axially elongated configurations, a similar configuration is suggested for $Cr(H_2O)_6^{2+}$. The Tutton salt of copper(II) examined by Lingafelter[36] shows two especially long Cu–O bonds; however three different Cu–O distances have been measured in this crystal. As mentioned previously, some other chromium(II) complexes studied crystallographically also show axial elongation.

Bersuker,[27,28] using simple group theoretical arguments, indicates the particular conformation (whether elongated or compressed) present in a tetragonal complex of a d^4 or d^9 ion may be determined from the relative intensities of the transitions to the states arising from the splitting of the $^5T_{2g}$ (in O_h) level. His arguments suggest that of the two components, the band with the greater intensity will be at the higher energy in the axially elongated complex. The compressed complex places the lower intensity band at the higher energy.

Holmes and McClure[7] found that the spectrum of $CuSO_4 \cdot 5H_2O$ definitely shows two bands and probably indicates three between 4000 and 20,000 cm.$^{-1}$. They located these bands by Gaussian analysis of crystal spectra at 10,500, 13,000, and 14,500 cm.$^{-1}$. The similarity between the spectra of $CrSO_4 \cdot 5H_2O$ (Table II) and $CuSO_4 \cdot 5H_2O$ is apparent. Assuming that the "alternative" assignment suggested by Holmes and McClure is correct, namely that the transition between the components of E_g is one of the peaks in the near-infrared absorption spectrum, the assignment becomes similar to the one we have assumed here for tetragonally distorted chromium(II) complexes, except of course that the spin multiplicity is 2 in the copper(II) system. Using the theoretical arguments of Bersuker[27,28] along with the Gaussian analysis of Holmes and McClure[7] for the $CuSO_4 \cdot 5H_2O$ spectrum, a compressed octahedral arrangement is predicted. This is contrary to fact and points to the questionable reliability of symmetry arguments alone in predicting even relative absorption intensities of centrosymmetric transition metal complexes.

With an argument similar[37] to the one presented in the discussion of the spectrum[3a] of $Mn(H_2O)_6^{3+}$, and using the data of Holmes and McClure[7] for $CuSO_4 \cdot 5H_2O$, Table III has been constructed. The results suggest tetragonally distorted Cu^{2+}(aq) and Cr^{2+}(aq) are 7–8 kcal./mole more stable electronically than the hypothetical regular octahedral complexes of these ions. The chromium(II) data were obtained from the positions of the three principal peaks found by a Gaussian analysis of the spectrum of Cr^{2+}(aq) (Figure 3). The details of the computer technique used for this analysis will be reported elsewhere.

TABLE III

TETRAGONAL PARAMETERS OF COPPER(II), CHROMIUM(II), AND MANGANESE(III) COMPLEXES

	$CuSO_4 \cdot 5H_2O$[a]	Cr^{2+}(aq)	Mn^{3+}(aq)[b]
Dq, cm.$^{-1}$	1300	1390	1860
Ds, cm.$^{-1}$	1710	1740	2530
Dt, cm.$^{-1}$	730	470	600
Stabilization, kcal.[c]	−7.4	−8.6	−12.7

[a] Data from ref. 7. [b] Reference 3a. [c] Calculated to equal $-2Ds + Dt$ for a high-spin $3d^4$ ion, the value represents the stabilization of the tetragonal configuration over that of a regular octahedral arrangement of ligands. See ref. 37 for definition of terms.

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[35] In an octahedral molecule of the AB_6 type, tetragonal distortion may occur by elongation of any of the *three* pairs of *trans* ligand–metal bonds (or by compression of four coplanar ligand–metal bonds). Thus the three configurations each with an identical energy are the equilibrium configurations between which minima exchange may occur.

[36] E. C. Lingafelter, ref. 2, p. 129.

[37] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y., 1962, p. 100.