was very slow, probably due to the insolubility of $CrCl_3$ in $AlCl_3$. The reaction had not gone to completion even after 1 week but had resulted in a concentration of divalent Cr sufficient for measuring the absorption spectrum.

The heights of the solutions in the cells were measured with a cathetometer at 227°. The volumes of the solutions were calculated using this measurement and the known volume of the cell. The cells were then placed in the spectrophotometer furnace. The details of this furnace have been described in a previous publication.[22]

The spectrophotometer used for the present study was a Cary Model 14H spectrophotometer with an optical arrangement having the following sequence: source, chopper, sample, monochromator, detector. This arrangement has the advantage of completely eliminating the black-body radiation from the sample and makes the instrument very useful for high temperature work.

The spectra of the 3d metal ions were determined at 227° where the pressure of $AlCl_3$ is 5.6 atm.[23] The spectrum of pure molten $AlCl_3$ was also obtained at the same temperature and this spectrum was subtracted from the other spectra.

The particular batch of optical cells employed in this work withstood 5.6 atm. of pressure. However, it must be emphasized that since the pressure of $AlCl_3$ increases rapidly with temperature and since the construction of the cells is not uniform it is important to take proper safety precautions. All operations were carried out behind shields and the cells were contained in suitably shielded containers while performing the optical measurements. These precautions are necessary because of the hazardous nature of liquid or gaseous $AlCl_3$.

---

(22) D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **66**, 57 (1962).

(23) JANAF, "Thermochemical Data, June 30, 1961," The Dow Chemical Co., Midland, Mich.

CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORY OF CHEMISTRY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

Spectral and Magnetic Properties of Chlorocuprates[1a]

BY WILLIAM E. HATFIELD AND T. S. PIPER[1b]

Received July 15, 1963

The optical spectra of four-, five-, and six-coordinate chloro complexes of copper(II) are interpreted in terms of the ionic model by using only one set of radial parameters. Magnetic susceptibilities of $[Co(NH_3)_6][CuCl_5]$ and $[Pt(NH_3)_4][CuCl_4]$ are reported.

The chloro complexes of copper(II) provide a unique opportunity to test the applicability of the ionic model for the description of the optical spectra of a series of complexes formed by a particular metal ion and a particular ligand. Probably with no other cation and single ligand do complexes with such a variety of geometries exist. Crystal structure determinations have shown that copper(II) is octahedrally coordinated with a tetragonal distortion in $CuCl_2$[2] and $CsCuCl_3$,[3] present in a trigonal bipyramid in $[Cr(NH_3)_6][CuCl_5]$,[4] constrained in a square coplanar arrangement of chlorides in $[Pt(NH_3)_4][CuCl_4]$,[5] and present in a flattened tetrahedron in Cs_2CuCl_4.[6,7] Some magnetic and spectral investigations of $CsCuCl_3$,[8] Cs_2CuCl_4,[8,9] and $[Co(NH_3)_6][CuCl_5]$[10] have been reported. Gruen and McBeth[11] have measured the spectrum of Cu(II) in the host lattices Cs_2ZnCl_4 and $CsCdCl_3$ and in the LiCl–KCl eutectic, and recently Furlani and Morpurgo[12] have studied the spectra of some tetrahalogenocuprates in solution. We now wish to show that the spectral data for all these compounds can be interpreted in a consistent manner by the ionic model with the use of only one set of radial parameters.

Magnetic susceptibilities of powdered $[Pt(NH_3)_4][CuCl_4]$ and $[Co(NH_3)_6][CuCl_5]$, which is isomorphous with $[Cr(NH_3)_6][CuCl_5]$,[4] are reported.

Experimental

The compounds used in the studies were prepared by conventional methods and were analyzed for nitrogen, hydrogen, and/or chloride before use. The analytical results indicated that the compounds were pure.

Optical spectra of mineral oil or hexachlorobutadiene mulls as well as those of crystals were obtained at room temperature or at 77°K. with a Cary Model 14 recording spectrophotometer. Reflectance spectra were obtained with a Beckman DU spectrophotometer equipped with the standard reflectance attachment using powdered magnesium oxide as a reflectance standard.

The salt $Rh(NH_3)_6CuCl_5$ was prepared in order to examine the visible spectral region obscured by the ${}^1A_1 \rightarrow {}^1T_1$ transition of the $Co(NH_3)_6^{+3}$ ion. No electronic transitions of the ion $CuCl_5^{-3}$ were found in this region.

The magnetic susceptibilities were determined by a previously described method[13] using $Hg[Co(CNS)_4]$ as a susceptibility standard.[14] Diamagnetic corrections were estimated from Pascal's constants.[15]

---

(1) (a) Supported by the National Science Foundation. A grant from the Kettering Foundation enabled us to construct a magnetic balance. (b) Alfred P. Sloan Foundation Fellow.

(2) A. F. Wells, *J. Chem. Soc.*, 1670 (1947).

(3) A. F. Wells, *ibid.*, 1662 (1947).

(4) M. Mori, Y. Saito, and T. Watanabe, *Bull. Chem. Soc. Japan*, **34**, 295 (1961).

(5) M. Bukorska and M. A. Porai-Koshits, *Crystallography*, **5**, 127 (1960); translated from *Kristallografiya*, **5**, 137 (1960).

(6) L. Helmholz and R. F. Kruh, *J. Am. Chem. Soc.*, **74**, 1176 (1952).

(7) B. Morosin and E. C. Lingafelter, *J. Phys. Chem.*, **65**, 50 (1961).

(8) B. N. Figgis and C. M. Harris, *J. Chem. Soc.*, 855 (1959).

(9) G. Felsenfeld, *Proc. Roy. Soc.* (London), **A236**, 506 (1956).

(10) M. Mori, *Bull. Chem. Soc. Japan*, **34**, 454, 1249 (1961).

(11) D. M. Gruen and R. McBeth, *Pure Appl. Chem.*, **6**, 23 (1963).

(12) C. Furlani and G. Morpurgo, *Theor. Chim. Acta*, **1**, 102 (1963).

(13) W. E. Hatfield, R. C. Fay, C. E. Pfluger, and T. S. Piper, *J. Am. Chem. Soc.*, **85**, 265 (1963).

(14) B. N. Figgis and R. Nyholm, *J. Chem. Soc.*, 4190 (1958).

(15) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 403. The susceptibility of $Co(NH_3)_6Cl_3$ was taken to be -87.7×10^{-6} c.g.s. from G. Foëx, "Constants Sélectionnées Diamagnétisme et Paramagnétisme," Masson and Co., Paris, 1957, p. 42.

Results and Discussion

TABLE I

MAGNETIC SUSCEPTIBILITY DATA FOR CHLOROCUPRATES

Compound	χ_M $\times 10^6$ c.g.s. units	$\chi_{M_{eff}}^{corr}$ $\times 10^6$ c.g.s. units	T, °K.	μ_{eff}, B.M.	θ, °K.
$[Co(NH_3)_6][CuCl_5]$	1257	1406	295.1	1.85	−8
	1952	2101	195.0		
	4720	4869	79.5		
$[Pt(NH_3)_4][CuCl_4]$	1079	1272	298.2	1.77	−10
	1700	1893	195.2		
	4260	4453	72.0		

The magnetic susceptibility data for $[Co(NH_3)_6]$-$[CuCl_5]$ and $[Pt(NH_3)_4][CuCl_4]$ are presented in Table I. Figgis and Harris[8] have studied the temperature dependence of the susceptibility of Cs_2CuCl_4 and $CsCuCl_3$ and have found that the data evidently obey the Curie–Weiss law, yielding moments of 1.99–2.00 and 1.93–1.95 B.M. for Cs_2CuCl_4 and $CsCuCl_3$, respectively. Mori[10] studied the temperature dependence of the susceptibility of $[Co(NH_3)_6][CuCl_5]$ in the liquid helium temperature range and found that the data obey the Curie–Weiss law down to *ca.* 2°K., yielding a moment of 1.47 B.M. with a Weiss constant of *ca.* −2.3°K. Mori attributed this low moment to the trigonal bipyramidal structure of chlorocuprate ion. However, our susceptibility measurements in the temperature range 77–300°K. give a normal magnetic moment. Note that we have included the correction for the temperature-independent paramagnetism of the cobalt cation[15] but not for that of the copper ion since the latter is but poorly known. The magnetic moment is in satisfactory agreement with that calculated (1.87 B.M.) from the average g value, 2.157 ± 0.002, measured by electron spin resonance; we thank Keith DeArmond, who kindly made this measurement for us.

The spin–orbit coupling constant, λ, for the pentachlorocuprate anion was estimated from the magnetic and spectral data and the expressions

$$g_{\|} = 2.0023$$

$$g_{\perp} = 2.0023(1 - 3\lambda/\Delta E)$$

From the isotropic g value which was measured by electron spin resonance to be 2.157, a value for $g_{\perp}$ of 2.234 was calculated. The value of $g_{\perp}$ and the observed energy of the $d_0 \leftarrow d_{\pm1}$ transition, ΔE, yielded a spin–orbit coupling constant of 402 cm.$^{-1}$.

The spectral data with band assignments for the chlorocuprates are presented in Table II.

The crystal spectrum of Cs_2CuBr_4 has been analyzed by Karipides and Piper.[16] Their results are directly applicable to the analysis of the polarized spectrum of Cs_2CuCl_4 since the two compounds are isomorphous.[7,17] Unfortunately the forbidden $d_{xy} \leftarrow d_{x^2-y^2}$ transition in $Cs_2(Zn,Cu)Cl_4$ was not observed, but the band at 8300 cm.$^{-1}$ was strongly polarized and is safely assigned to the $d_{xy} \leftarrow d_{z^2}$ transition.

TABLE II

SPECTRAL DATA FOR THE CHLOROCUPRATES

Compound	Maxima, cm.$^{-1}$ Observed	Predicted	Assignment
Cs_2CuCl_4	8,300[a]	...	
	9,000[b]	8,300	$d_{xy} \leftarrow d_{z^2}$
	~4,500[c]	4,100	$d_{xy} \leftarrow d_{xz}, d_{yz}$
$[Co(NH_3)_6][CuCl_5]$	~27,000[d]	...	Charge transfer
	10,400[e]	9,540	$d_0 \leftarrow d_{\pm1}$
	8,200[e]	6,500	$d_0 \leftarrow d_{\pm2}$
$[Pt(NH_3)_4][CuCl_4]$[e]	24,900	...	Charge transfer
	14,300	14,950	$d_{x^2-y^2} \leftarrow d_{xy}$
	13,100	12,990	$d_{x^2-y^2} \leftarrow d_{\pm1}$
	~10,900	11,280	$d_{x^2-y^2} \leftarrow d_{z^2}$
$CsCuCl_3$	24,600 19,800[f]	...	Charge transfer
	11,800[g]	11,290	$d_{x^2-y^2} \leftarrow d_{\pm1}$
	11,000[g]	11,100	$d_{x^2-y^2} \leftarrow d_{xy}$
	...	4,090	$d_{x^2-y^2} \leftarrow d_{z^2}$
$CuCl_2$[h]	12,200	11,300	$d_{x^2-y^2} \leftarrow d_{\pm1}$
		10,860	$d_{x^2-y^2} \leftarrow d_{xy}$
	...	5,790	$d_{x^2-y^2} \leftarrow d_{z^2}$

[a] Single crystal of $Cs_2(Cu,Zn)Cl_4$. [b] Mull of Cs_2CuCl_4. [c] Ref. 11. [d] Ref. 10. [e] Mull at 77°K. [f] G. Basu and R. L. Belford, private communication. [g] P. Day, *Proc. Chem. Soc.*, 18 (1964); see footnote 23. [h] Reflectance spectrum.

One set of radial parameters, ρ_2 and ρ_4, with values of 6620 and 7780 cm.$^{-1}$, respectively, defined for a Cu–Cl distance of 2.2 Å. were used to fit the spectral data for all of the compounds in Table II. These parameters were adjusted by the $1/R^{n+1}$ proportionality to fit the Cu–Cl distances in the other compounds. The adjusted parameters are given in Table III. The ionic model equations for the splitting of the 3d levels in the fields of the various symmetries were taken from the existing literature. Piper and Karipides[16] have reported equations for the splitting in the D_{2d} field, Piper and Carlin[18] for the tetragonal field, Belford[19] for the square coplanar field, and Ballhausen[20] for the trigonal bipyramidal field.

Since the Cu–Cl distance in $[Pt(NH_3)_4][CuCl_4]$ is unknown, the radial parameters were used directly to predict the absorption spectrum which is listed in Table II with the values predicted for the other geometries.

Our qualitative experiments indicated that the energy of the $d_{xy} \leftarrow d_{z^2}$ transition is dependent upon the concentration of copper in the $Cs_2(Cu,Zn)Cl_4$ crystal. This observation is in agreement with the ionic model which predicts that this band should occur at higher energy the more the deviation from the pure tetrahedral field. For purely tetrahedral $CuCl_4^{-2}$, which would have an average polar angle, α,[16] of 54.7°, an absorption band would be expected at about 5700 cm.$^{-1}$, whereas the band was observed at 9000 cm.$^{-1}$ in Cs_2CuCl_4, which has an average polar angle of 62°, and at 8300 cm.$^{-1}$ in the $Cs_2(Cu,Zn)Cl_4$ crystal that we used. Although α for Cs_2ZnCl_4 is not known, it is not expected to deviate much from the tetrahedral

---

(16) A. G. Karipides and T. S. Piper, *Inorg. Chem.*, **1**, 920 (1962).

(17) B. Morosin and E. C. Lingafelter, *Acta Cryst.*, **13**, 807 (1960).

(18) T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, **33**, 1208 (1960).

(19) R. L. Belford, M. Calvin, and G. Belford, *ibid.*, **26**, 1165 (1957).

(20) C. J. Ballhausen, *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.*, **29**, No. 4 (1954).

TABLE III

RADIAL PARAMETERS FOR THE CHLOROCUPRATES

Compound	Structure	Cu–Cl bond distance, Å.	Adjusted radial parameter ρ_2, cm.$^{-1}$	ρ_4, cm.$^{-1}$
Cs_2CuCl_4	Flattened tetrahedron	Average 2.2	6620	7780
$[Pt(NH_3)_4][CuCl_4]$	Square coplanar	Unknown	. . .	. . .
$[Co(NH_3)_6][CuCl_5]$	Trigonal bipyramid	Axial 2.32	5798	6240
		Equatorial 2.35	5579	5852
$CsCuCl_3$[a]	Distorted octahedron	Axial 2.65	3891	3210
		Equatorial 2.29	6030	6660
$CuCl_2$	Distorted octahedron	Axial 2.95	2821	1878
		Equatorial 2.3	5951	6516

[a] The rhombic distortion in this compound has been ignored.

value. Thus, our results indicate that the tetrahedral instability of the copper ion leads to a strong distortion even in the dilute crystal and that the distortion increases with increasing concentration of copper ion.

The nearly comparable intensities of the two bands in the spectrum of $[Co(NH_3)_6][CuCl_5]$ violate the selection rules for D_{3h}: $d_0 \nleftrightarrow d_{\pm 1}$, $d_0 \leftrightarrow d_{\pm 2}$. Bader and Westland[21] found that the $d_0 \leftarrow d_{\pm 1}$ transition is by far the least intense band in the spectrum of $MoCl_5$. However, this work has been questioned.[22] It must be that the close proximity of the $d_{\pm 2}$ and $d_{\pm 1}$ levels in the pentachlorocuprate ion results in considerable spin–orbit mixing and that the selection rules are broken down. The predicted energy of the $d_0 \leftarrow d_{\pm 2}$ transition for $CuCl_5^{-3}$ does not agree very well with the observed. There remains the possibility not excluded by our results that the $d_0 \leftarrow d_{\pm 2}$ transition lies to lower energy outside the range of our spectral studies, and that the observed band is the $d_{\pm 1}$ level split by spin–orbit coupling and a dynamic Jahn–Teller effect.

Conclusion

For many years the ionic model has provided the framework of spectral analysis. For an ion such as Ni^{2+} in a weak octahedral field a satisfactory fit of the numerous experimental bands and lines can be obtained with the gas phase term values and a single parameter Dq of the ionic model; marked improvement results when one of the Slater parameters is also fitted. However, the ionic model predicts Dq to be about one-fourth of the observed value. From these observations we concluded that the angular parts of the wave functions of the chromophoric electrons are very close to the d-orbital but that the radial functions are strongly perturbed in the ligand field.

These observations gave us reason to hope that the spectra of complexes of a given metal ion and ligand with a variety of geometries could be interpreted successfully in the ionic model. If this hope were fulfilled then chemists would be spared the onerus task of a full molecular orbital treatment of every new complex.

In applying the ionic model one difficult point remains: if the radical parameters are to be taken as empirical parameters, how can we proceed with complexes in which the slight variations in metal–ligand distances preclude direct carry-over of the radial parameters? We have assumed that small displacements can be represented by the proportionality to $1/R^{n+1}$ as predicted in the ionic model. However, we have not made corrections for groups beyond the first coordination sphere. The effect of these groups undoubtedly can be well approximated by the ionic model and hence can safely be ignored relative to the stronger interaction of the ligands in the first coordination sphere.

The success of this procedure is attested to by the fact that bands in a 9000–14,300 cm.$^{-1}$ interval are fitted usually to within 10%.[23]

---

(21) R. F. W. Bader and A. D. Westland, *Can. J. Chem.*, **39**, 2306 (1961).

(22) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 275.

(23) NOTE ADDED IN PREPARATION.—E. A. Boudreaux has recently published a study of the magnetic susceptibilities of chlorocuprates in *Trans. Faraday Soc.*, **59**, 1055 (1963). Also, Peter Day has published in *Proc. Chem. Soc.*, 18 (1964), an analysis of the spectra of four-, five-, and six-coordinate halocuprates which is similar to the one given here.