Experimental Section

The experimental procedures were outlined previously.[2] A 206.2-nm iodine lamp[31] was used for the photolyses, and the formation of P_2H_4 was monitored by its increase in UV absorption at 235 nm. The correct value for the extinction coefficient of P_2H_4 at 235 nm is 2174 M^{-1} cm^{-1}, base 10 (205 atm^{-1} cm^{-1}, base *e*), and not the value given in ref 2. The extinction coefficients of PH_3 and NH_3 at 206 nm were found to be 23 and 33 atm^{-1} cm^{-1}, base *e*, respectively. These values are comparable to the extinction coefficients reported previously.[16-18] In general, the error limits for the quantum yields were estimated on the basis of a 20% variation in the lamp flux and a 10% error in the determination of the extent of NH_3 photolysis in the actinometer by gas chromatographic analysis of the H_2 formed. Each quantum yield plot comprised at least six data points. A linear plot was constructed by a least-squares analysis. Correlation coefficients for the slope of each plot exceeded 0.92 in most cases. The relative amounts of P_n formed were determined from the optical density at 206 nm after the gases were removed from the photolysis cell.

An improved procedure was developed for the determination of the amount of H_2 formed by PH_3 photolysis. Both ends of the sample loop for the gas chromatograph were evacuated before the gas mixture was transferred to the loop. Also 100 torr of Ar was added to the H_2 before transfer to the sample loop so that there would be a pressure differential and therefore reproducible transfer of an aliquot of the gas mixture each time.

The sampling procedure of Toupance[32] was used to enhance the sensitivity of the gas chromatographic N_2 analysis. The NH_3 and PH_3 remaining after the photolysis was condensed with liquid N_2, and 70 torr of He was added to the cell. The noncondensible gases were then transferred to an evacuated coil (530 cm^3), which was attached to the sample loop of the gas chromatograph. A 2-L reservoir containing 1 atm of He attached to the other end of the coil was opened, and the gases in the coil were compressed into the sample loop. In control experiments it was determined that 90% of the contents of the photolysis cell was transferred to the sample loop of the gas chromatograph by this procedure.

Photolyses were performed at 227 and 157 K by immersing the cell, except for one window, in a chlorobenzene or ether slush bath, respectively. It was not feasible to use the merry-go-round in these studies so the actinometry was done prior to and after a series of low-temperature photolyses. The deviations in the lamp flux in each series of experiments did not exceed 10%.

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Registry No. Phosphorus, 7723-14-0; phosphine, 7803-51-2.

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(31) Hartreck, P.; Reeves, R. R., Jr.; Thompson, B. A. *Z. Naturforsch., A* **1964**, *19A*, 2-6.

(32) Toupance, G., These d'Etat ès-Sciences Physiques, Université Paris 6, 1973, pp 146-148.

Intermetallic Charge-Transfer Spectra of Copper(I)-Metal(III) Centers in Doped Crystals of $CsMgCl_3$

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Abstract: When crystals of $CsMgCl_3$ are co-doped with small concentrations of Cu(I) and Cr(III), Mo(III), Ru(III), or Rh(III), charge-compensation stabilized Cu(I)-M(III) dimers are formed in the linear chain lattice. The absorption spectra of the crystals containing the Cu(I)-M(III) impurity centers exhibit intense, strongly polarized bands that cannot be attributed to electronic excitations localized on either Cu(I) or M(III). These bands are assigned to intermetallic charge-transfer (IT) transitions where an electron from Cu(I) is transferred to M(III). In some cases more than one IT transition is observed. The spectral properties of the Cu(I)-M(III) centers are compared to those of the analogous Li(I)-M(III) centers. A relatively simple theoretical treatment is presented that accounts for many of the features in the IT spectra of the Cu(I)-M(III) centers.

It has been demonstrated in a number of spectroscopic studies that crystals of $CsMX_3$ salts such as $CsMgCl_3$ incorporate a wide variety of trivalent ions in low concentrations as substitutional impurities. These host materials adopt the linear chain $CsNiCl_3$ structure in which the MX_6^{4-} octahedra share opposite faces to form infinite linear chains of the stoichiometry, $[MX_3^-]_n$.[1,2] The cesium ions occupy positions between the chains and balance the anionic charge. Trivalent impurities enter the lattice in a manner that preserves the overall charge balance of the $[MX_3^-]_n$ chains.[3-7] As a result the trivalent impurities cluster as pairs in association with a divalent ion vacancy. This produces linear M(III)-vacancy-M(III) centers which are electrostatically equivalent to three divalent ions. The presence of small monovalent ions provides an alternate mode by which trivalent ions can enter the $[MX_3^-]_n$ chains. A trivalent ion and a monovalent ion enter adjacent divalent sites to give a M(I)-M(III) center that is electrostatically equivalent to two divalent ions. The EPR spectra of crystals doped with chromium(III) indicate that M(I)-Cr(III) centers are formed when lithium, sodium, or copper(I) ions are present.[5,7] In the course of the EPR studies it was noted that crystals of $CsMgCl_3$ and $CsCdBr_3$ containing the Cu(I)-Cr(III) centers exhibited an unusual coloration. This observation prompted an investigation of the electronic spectrum of the Cu(I)-Cr(III) system. At low

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(1) McPherson, G. L.; Kistenmacher, T. J.; Stucky, G. D. *J. Chem. Phys.* **1970**, *57*, 815-24.

(2) McPherson, G. L.; McPherson, A. M.; Atwood, J. L. *J. Phys. Chem. Solids* **1980**, *41*, 495-9.

(3) McPherson, G. L.; Henling, L. M. *Phys. Rev. B: Solid State* **1977**, *16*, 1889-92.

(4) Henling, L. M.; McPherson, G. L. *Phys. Rev. B: Solid State* **1977**, *16*, 4756-60.

(5) McPherson, G. L.; Heung, W.; Barraza, J. J. *J. Am. Chem. Soc.* **1978**, *100*, 469-75.

(6) McPherson, G. L.; Varga, J. A.; Nodine, M. H. *Inorg. Chem.* **1979**, *18*, 2189-95.

(7) McPherson, G. L.; Devaney, K. O. *J. Phys. C: Solid State Phys.* **1980**, *13*, 1735-43.

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temperatures the absorption spectra of the crystals doped with Cu(I) and Cr(III) exhibit a series of intense bands that are strongly polarized along the direction of the $[MX_3^-]_n$ chains (the crystallographic *c* axis). These absorptions require the simultaneous presence of both ions and cannot be assigned to electronic transitions localized on either Cu(I) or Cr(III). Crystals containing the analogous Li(I)-Cr(III) centers do not exhibit these unusual features. It appears that the highly polarized bands result from intermetallic charge-transfer (IT) transitions where an electron is transferred from copper(I) to chromium(III). In subsequent investigations it was observed that $CsMgCl_3$ crystals in which copper(I) was co-doped with molybdenum(III), rhodium(III), or ruthenium(III) also exhibited strongly polarized absorptions, which can be attributed to IT transitions. This paper describes the IT spectra of the Cu(I)-M(III) impurity centers in the $CsMgCl_3$ crystals.

Experimental

Preparation of Materials. The host material, $CsMgCl_3$, was prepared according to a previously reported procedure.[1] Doped samples were obtained by adding small amounts of the appropriate metal halides to the host material and fusing the resulting mixtures under vacuum. The chlorides of chromium(III), molybdenum(III), rhodium(III), and ruthenium(III) were obtained commercially (Alfa Inorganics). Copper(I) chloride was prepared by the reduction of the copper(II) chloride. Crystals were grown from the melt (in vycor ampules) by the Bridgeman method. The apparatus and procedure have been previously described.[8] The $CsMgCl_3$ crystals are very hygroscopic and must be handled in a dry atmosphere.

Crystal Spectra. Samples of the doped crystals suitable for absorption spectroscopy were obtained by carefully cleaving the crystalline boules that were produced by the Bridgeman procedure. The $CsMgCl_3$ crystals have a pronounced tendency to cleave parallel to the crystallographic *c* axis. When a razor blade was used it was possible to obtain flat plates in which the *c* axis was contained in the plane of the plate. The direction of the *c* axis was then determined with the aid of a polarizing microscope. The oriented crystal was mounted on the sample holder of an Air Products Displex cryostat with "cryocon" heat conducting grease. The sample and holder were then attached to the cryostat and lowered into the optical path of a Cary 14 spectrophotometer. Polarized spectra were obtained by inserting Glan-Thompson polarizers into the sample and reference beams. Spectra were recorded with the electric vector of the light polarized either parallel ($\parallel$) or perpendicular ($\perp$) to the *c* axis of the crystal. Most of the spectra were recorded with the sample block cooled to the minimum operating temperature of the Displex System, approximately 10 K. The actual crystal temperature, however, may have been a few degrees higher.

Results and Discussion

M(I)-M(III) Centers in $CsMgCl_3$ Crystals. Several $CsMX_3$ salts are suitable materials for the formation of M(I)-M(III) centers; however, $CsMgCl_3$ is the preferred host lattice for spectral studies in the visible and UV regions. In the other linear chain salts such as $CsMgBr_3$, $CsCdBr_3$, and $CsMgI_3$, the halide-to-metal charge-transfer (LMCT) absorptions will occur at significantly lower energies. These charge-transfer bands are quite intense and will obscure most other spectral features. Thus, the spectrum of a given M(I)-M(III) center can be characterized over the widest energy range in the $CsMgCl_3$ lattice. The basic geometry of the M(I)-M(III) centers is imposed by the linear chain structure of the host material, although the incorporation of the impurity ions may cause some local lattice distortions. A schematic drawing of a M(I)-M(III) center is shown in Figure 1. If the host lattice is viewed as a rigid, spectroscopically inert matrix, the M(I)-M(III) center can be described as a dimer composed of two octahedral complexes joined at a common face. This $[M^{I}M^{III}X_9]^{5-}$ dimer has C_{3v} symmetry with the threefold axis passing through the M(I) and M(III) ions. An approximate molecular geometry can be extracted from the known structural properties of the host material. In $CsMgCl_3$ the separation between adjacent divalent ion sites is 3.09 Å and the Mg-Cl-Mg angle is 76.6°.[1] From the perspective of an electron-transfer process, the M(I) and M(III) centers are inner-sphere complexes since the M(I) and M(III) ions share three halide ions as common ligands. The direction of electron movement in a charge transfer from M(I) to M(III) corresponds to the threefold axis of the M(I)-M(III) center and is parallel to the crystallographic *c* axis.

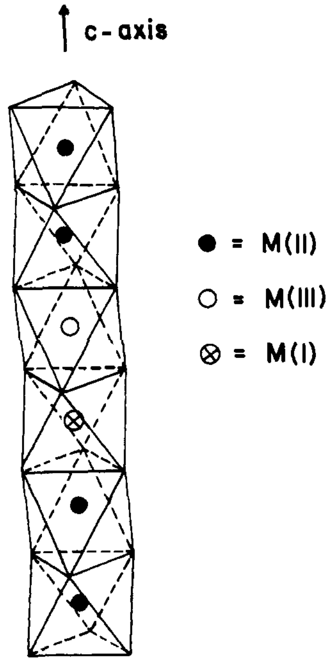

Figure 1. Schematic diagram of a $[MX_3]_n$ chain containing a M(I)-M(III) impurity center. The halide ions occupy the corners of the octahedra.

The ability of the $CsMX_3$ salts such as $CsMgCl_3$ to incorporate a wide range of impurities makes it possible to compare the spectroscopic properties of structurally similar centers containing a number of different ions. This feature is particularly valuable in the present study since the spectra of the crystals containing Cu(I)-M(III) centers may be directly compared to those of crystals doped with M(I)-M(III) centers formed from alkali metal ions such as lithium or sodium that do not exhibit IT absorption.

Spectra of Crystals Containing M(I)-M(III) Centers. The spectra of $CsMgCl_3$ crystals containing Cr(III) co-doped with either Cu(I) or Li(I) are shown in Figure 2. In spite of the structural similarity between the Cu(I)-Cr(III) and Li(I)-Cr(III) centers the spectral properties of the two systems differ dramatically. The spectrum of the crystal containing Cr(III) and Li(I) consists of bands that are readily assigned to the ligand-field transitions of an octahedral chromium(III) complex. The ligand-field bands are similar in energy and general appearance to those reported for solid $CrCl_3$[9] and Cr(III) doped in crystals of Na_2CsYCl_6.[10] All of these materials contain Cr(III) ions surrounded by octahedral arrangements of chloride ions. The ligand-field bands of the Li(I)-Cr(III) center are partially polarized (intensity ratios, $I_\parallel/I_\perp$, range between 0.8 and 2) which indicates that the $CsMgCl_3$ lattice imposes a significant noncubic (trigonal) component on the ligand field.

The spectrum of the $CsMgCl_3$ crystal doped with Cu(I) and Cr(III) contains a number of strong absorptions that cannot be attributed to the ligand-field transitions of the Cr(III) ion. The absorptions are strongly polarized along the crystallographic *c* axis (for most of these bands, $I_\parallel/I_\perp > 10$) and are considerably more intense than the ligand-field transitions. Crystals of $CsMgCl_3$ doped with Cu(I) show no absorption in the 10000 to 30000-cm^{-1} region which establishes that the strong absorptions require the simultaneous presence of the two ions. All of these properties are consistent with the intermetallic charge-transfer (IT) transitions

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(8) McPherson, G. L.; Sindel, L. J.; Quarls, H. F.; Frederick, C. B.; Doumit, C. J. *Inorg. Chem.* **1975**, *14*, 1831-4.

(9) Wood, D. L.; Ferguson, J.; Knox, K.; Dillon, J. F., Jr. *J. Chem. Phys.* **1963**, *39*, 890-8.

(10) Schwartz, R. W. *Inorg. Chem.* **1976**, *15*, 2817-22.

Table I. Energies and Assignments for the Ligand-Field Spectra of the $CsMgCl_3$ Crystals Containing Li(I)–M(III) Centers

M(III)	assignment	Li^I–$M^{III}/CsMgCl_3$		comparable $M^{III}Cl_6$ Complex	
		∥	⊥		
Cr(III)	$^4A_2 \rightarrow {}^4T_2$	13 700	13 500	12 800	$Cr(III)/Cs_2NaYCl_6$[10]
	$\rightarrow {}^2E$		14 300	14 430	
	$\rightarrow {}^2T_1$	14 820	14 820	15 010	
	$\rightarrow {}^4T_1$ (F)	18 900	18 600	18 200	
	$\rightarrow {}^2T_2$	19 800	19 800	~20 000	
	$\rightarrow {}^4T_1$ (P)	29 000	29 000	28 400	
Mo(III)	$^4A_2 \rightarrow {}^2E, {}^2T_1$			9 500	K_3MoCl_6/9 M HCl[12]
	$\rightarrow {}^2T_2$	14 400		14 800	
	$\rightarrow {}^4T_2$	19 000	20 200	19 400	
	$\rightarrow {}^4T_1$	23 600	24 400	24 200	
Ru(III)	$^2T_2 \rightarrow {}^2A_2$	19 000	19 400	19 200	K_2RuCl_5/12 M HCl[13]
Rh(III)	$^1A_1 \rightarrow {}^1T_1$	20 100	19 800	19 300	Na_3RhCl_6/4 M HCl[14]
	$\rightarrow {}^1T_2$	24 100	24 500	24 300	

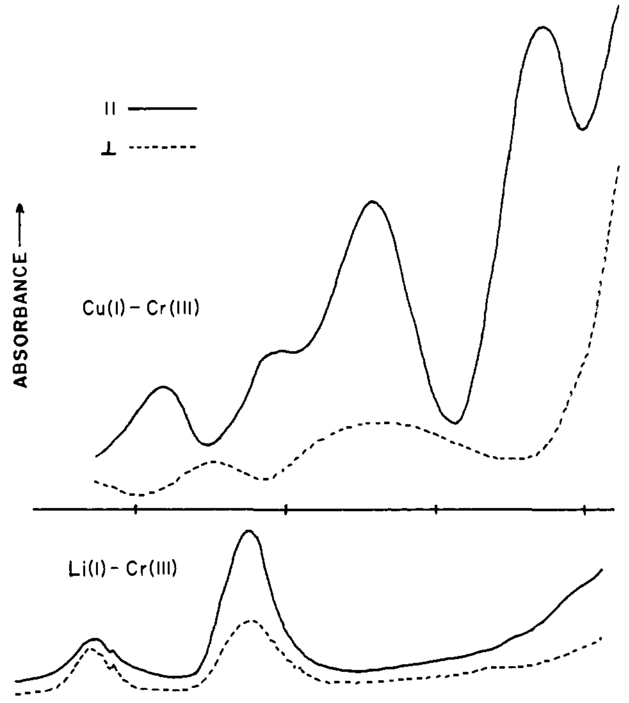

Figure 2. Polarized spectra of $CsMgCl_3$ crystals containing Cr(III) co-doped with Cu(I) (top) and Li(I) (bottom). The solid lines represent the spectra recorded with the electric vector of the light polarized parallel (∥) to the crystallographic *c* axis, while the dotted lines correspond to the perpendicular polarization (⊥). The spectrum of the crystal containing Cu(I) and Cr(III) was recorded at approximately 10 K. The spectrum of the crystal doped with Li(I) and Cr(III) was recorded at 77 K.

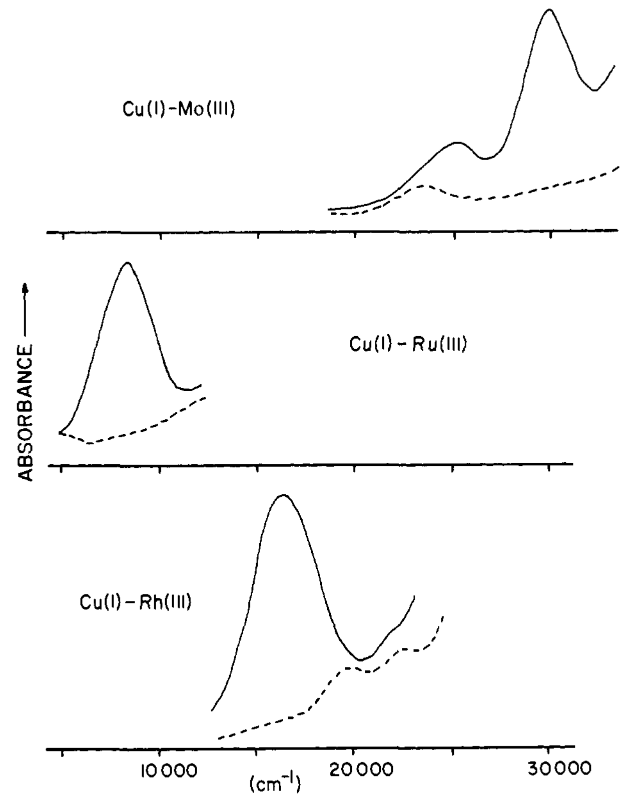

Figure 3. Portions of the polarized spectra of the $CsMgCl_3$ crystals containing the Cu(I)–M(III) centers which show the bands assigned to IT transitions. The solid lines represent spectra recorded with the electric vector of the light polarized parallel (∥) to the crystallographic *c* axis, while the dotted lines correspond to the perpendicular polarization (⊥). These spectra were obtained at approximately 10 K.

of an inner-sphere redox complex. The selection rule for charge-transfer absorption usually requires the transition moment to be aligned along the direction of charge movement.[11] This fits the observed band polarizations.

One might expect IT absorptions in the spectra of Cu(I)–M(III) centers whenever the trivalent ion can behave as an electron acceptor. To explore this possibility a number of $CsMgCl_3$ crystals were prepared in which different trivalent metals (Mo(III), Ru(III), and Rh(III)) were co-doped with copper(I). Crystals containing the same trivalent metals co-doped with lithium were also prepared. The absorption spectra of both groups of crystals were investigated. Almost all of the absorptions that appear in the spectra of the crystals containing the Li(I)–M(III) centers can be assigned to the ligand-field transitions of the trivalent ion. The spectral properties of the Li(I)–M(III) centers are very similar to those reported for other systems containing octahedral $[M^{III}Cl_6]$ groups.[12-14] The band energies and assignments for the ligand-field transitions are presented in Table I. The data for some previously studied octahedral hexachloro complexes are included for comparison.

As expected the spectra of the crystals with the trivalent ions co-doped with copper(I) exhibit additional absorption bands that can be attributed to IT transitions. These bands, shown in Figure 3, are polarized along the *c* axis ($I_{\parallel}/I_{\perp} > 10$) and are not present in the spectra of the lithium-containing crystals. Although it is not possible to determine the band intensities quantitatively without knowing the actual concentrations of the different centers present in a doped crystal, it does appear that the IT absorptions are

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[11] Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391–444.

[12] Furlani, C.; Piovesana, O. *Mol. Phys.* **1965**, *9*, 341–7.

[13] Jorgensen, C. K. *Acta Chem. Scan.* **1956**, *10*, 518–34.

[14] Jorgensen, C. K. *Acta Chem. Scand.* **1956**, *10*, 500–17.

Table II. Calculation of IT Energies of the Cu(I)–M(III) Centers

M(III)	χ(optical)	10*Dq* (cm^{-1})	*B* (cm^{-1})	Δ*E* (cm^{-1})	M(II) config	Δ*P* (cm^{-1})	IT energy (cm^{-1}) calcd	IT energy (cm^{-1}) obsd
Cr(III)	1.9	13 600	500	12 000	$t_{2g}{}^3e_g$ ($S = 2$)	−2 (4500)	16 600	15 800
					$t_{2g}{}^4$ ($S = 1$)	+2 (4500)	21 000	19 500
								22 800
					$t_{2g}{}^2e_g{}^2$ ($S = 2$)	−2 (4500)	29 600	28 500
					$t_{2g}{}^3e_g$ ($S = 1$)	+2 (4500)	34 600	
Mo(III)	1.7	19 600	400	18 000	$t_{2g}{}^4$ ($S = 1$)	+2 (3500)	25 000	25 300
					$t_{2g}{}^3e_g$ ($S = 2$)	−2 (3500)	30 600	30 000
Ru(III)[a]	2.1	[20 800]	[310]	6 000	$t_{2g}{}^6$ ($S = 0$)	(+2/3) (2400)	7 800	8 500
					$t_{2g}{}^5e_g$ ($S = 1$)	(−2/3) (2400)	25 200	
Rh(III)	2.4	20 800	310	−3 000	$t_{2g}{}^6e_g$ ($S = {}^1/_2$)	(2400)	15 400	16 400

[a] The bracketed parameters are assumed to be the same as those for Rh(III).

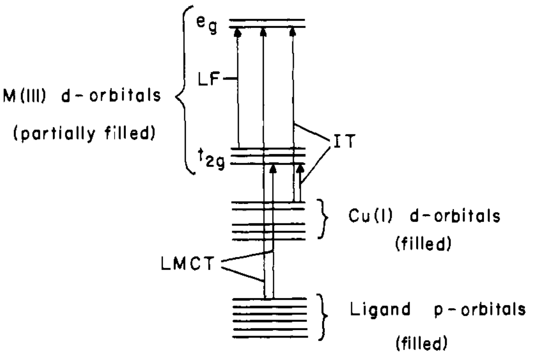

Figure 4. An approximate energy level diagram showing the relative positions of the M(III) d orbitals, Cu(I) d orbitals, and ligand (chloride) p orbitals. The ligand-field (LF), intermetallic charge-transfer (IT), and ligand-to-metal charge-transfer (LMCT) transitions are indicated.

considerably more intense than the ligand-field transitions. (The intensities of the ligand-field transitions can be observed in the perpendicular polarization where the IT absorptions do not appear.)

The only significant spectral feature with no clear assignment appears in the spectra of the $CsMgCl_3$ crystals containing Ru(III) with Li(I) and Ru(III) with Cu(I). A band occurs at 14 000 cm^{-1} that cannot be attributed to a ligand-field transition of the Ru(III) ion or a Cu(I) to Ru(III) charge-transfer absorption. There is no obvious explanation for this band. Under the preparation conditions it is possible that more than one oxidation state of ruthenium is present in the doped crystals.

Cu(I) to M(III) Charge Transfer. In general, the spectral properties of the Cu(I)–M(III) centers are explainable in terms of the simple energy level diagram shown in Figure 4. The IT transitions result from the excitation of an electron from the filled 3d shell of the Cu(I) ion into the partially filled d shell of the M(III) ion. The energies of the M(III) ion d orbitals should be significantly dependent on the nature of the trivalent metal. For a series of transition metals in the same period and oxidation state, the d-orbital energies should drop as the atomic number increases. The energy required for an IT transition will depend not only on the energy separation between the d orbitals of the Cu(I) ion and the d orbitals of the M(III) ion but also on the number of d electrons present on M(III).

It is possible to treat the intermetallic charge-transfer transitions of the Cu(I)–M(III) centers by the approach developed by Jorgensen for the analysis of ligand-to-metal charge-transfer (LMCT) spectra.[15-17] In this approach, the energy difference between the filled ligand orbitals (Cu(I) d orbitals) and the t_{2g} set of metal d orbitals is assumed to be proportional to the difference in optical electronegativity between metal and ligand. For a Cu(I)–M(III) center the following expression would apply.

$$\Delta E\ (\mathrm{cm}^{-1}) = 30000(\chi_c - \chi_m)$$

The energy of an IT transition where the transferred electron enters the t_{2g} set of M(III) d orbitals can be calculated from the expression shown below, where ΔP represents the change in pairing energy when M(III) is reduced to M(II).

$$\mathrm{IT} = \Delta E + \Delta P$$

If the transferred electron enters the e_g set of M(III) d orbitals the IT energy is then expressed as follows.

$$\mathrm{IT} = \Delta E + 10Dq + \Delta' P$$

The quantity $10Dq$ corresponds to the energy difference (ligand-field splitting) between the t_{2g} and e_g sets of the M(III) d orbitals.

In order to actually calculate the IT energies for the Cu(I)–M(III) centers reasonable estimates of the optical electronegativities, pairing energies, and ligand-field splitting must be made. These data are presented in Table II. The optical electronegativities of the metal ions are taken from the list compiled by Lever.[18] These optical electronegativities assume that the metal ions act as electron acceptors. In the Cu(I)–M(III) centers the copper(I) ion behaves as an electron donor rather than an electron acceptor. By trial and error it was determined that a χ_c value of 2.3 produced a good fit of the observed data. It seems quite reasonable that the value of 2.3 corresponds to the optical electronegativity reported for the copper(II) ion.[18] The reported optical electronegativity referres to the process in which an electron is transferred to a copper(II) ion to give a copper(I) ion. In the IT absorptions of the Cu(I)–M(III) centers the reverse of this process takes place. The ligand-field splittings (10Dq) for Cr(III), Mo(III), and Rh(III) are determined from the band energies of the spin-allowed transitions observed in the spectra of the crystals containing the trivalent ions and lithium, using the energy level expressions given by Lever.[18] The spectrum of the crystal doped with Ru(III) and Li(I) shows only one ligand field band and the energy of the transition is not a simple function of $10Dq$. It is reasonable to assume that Ru(III) should be similar to Rh(III) in terms of spectral parameters such as $10Dq$, B, and C. The pairing energies of the ions, P, are somewhat more difficult to establish. According to Jorgensen the pairing energy of an ion is related to the interelectronic repulsion parameters, B and C.[17]

$$P = (7/6)[(5/2)B + C]$$

Unfortunately, the evaluation of these parameters from observed spectral energies is often not straightforward. For Cr(III) the value of 500 cm^{-1} for B is extracted from the positions of the three spin-allowed transitions,[19] and the C parameter is calculated by assuming a C/B ratio of 5.25.[10] Similarly, the B value of 400 cm^{-1} for Mo(III) is calculated from the energies of the two spin-allowed transitions. The value of 2000 cm^{-1} for C is computed from the energy of the spin-forbideen ($^4A_2 \rightarrow {}^2T_2$) transition according to the energy level expression given by Lever.[18] For

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(15) Jorgensen, C. K. *Solid State Phys.* **1962**, *13*, 376–462.
(16) Jorgensen, C. K. *Mol. Phys.* **1963**, *6*, 43–7.
(17) Jorgensen, C. K. *Prog. Inorg. Chem.* **1970**, *12*, 101–58.
(18) Lever, A. B. P. "Inorganic Electronic Spectroscopy"; Elsevier: New York, 1968.
(19) Witzke, H. *Theor. Chim. Acta* **1971**, *20*, 171–185.
(20) Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94–100.

Rh(III) the value of B is computed from the transition energies, and the free ion C/B ratio of 4.0 is used to calculate C. Clearly, the procedures used to compute the spin-pairing energies for the trivalent metals are tenuous at best; however, the resulting P values seem reasonable.[17] Once the ligand-field splittings and spin-pairing energies are determined it is a straightforward procedure to compute the charge-transfer energies.[17,18] Depending on the number of d electrons present on the M(III) ion, the transferred electron may be able to enter either the t_{2g} or the e_g set of metal d orbitals so that several different IT transitions may occur. This appears to be the case with the centers containing the d^3 ions, Cr(III) and Mo(III), where the spectra show more than one distinct IT absorption. With a d^3 ion a ${t_{2g}}^4$ configuration will result when the transferred electron enters the t_{2g} orbitals while entry into the e_g orbitals will produce a ${t_{2g}}^3e_g$ configuration. With the assumption that the usual spin selection rule is operational, the transferred electron must enter the half-filled t_{2g} orbitals with a spin that is antiparallel to the three electrons already present. This gives the system a total spin of 1. The incoming electron can enter the empty e_g orbitals with parallel or antiparallel spin to give ${t_{2g}}^3e_g$ configurations with total spins of 1 or 2. It is possible for the transferred electron to enter either the t_{2g} or the e_g orbitals in the Cu(I)–Ru(III) center; however, the spectrum shows only one IT band. Presumably, the other IT bands are obscured by the intense chloride-to-ruthenium charge-transfer (LMCT) absorption that begins between 20 000 and 25 000 cm^{-1}. Only one IT transition is possible for the Cu(I)–Rh(III) center since the t_{2g} orbitals of the rhodium(III) ion are completely filled (low-spin d^6 ion).

The results of the computations for all of the Cu(I)–M(III) centers are presented in Table II. The agreement between the observed and calculated energies is remarkably good in view of the relatively unsophisticated nature of the theoretical treatment. It is interesting that in the lowest energy IT transition of the Cu(I)–Cr(III) center the transferred electron enters the e_g orbitals to produce a "high-spin" chromium(II) ion while in the lowest energy IT transition of the Cu(I)–Mo(III) center the transferred electron enters the t_{2g} orbitals to give "low-spin" molybdenum(II). This observation is consistent with the general trend that 3d transition-metal ions form high-spin complexes with weak field ligands such as chloride while the 4d and 5d transition-metal ions invariably form low-spin complexes.

The treatment based on Jorgensen's theoretical analysis provides a reasonably good overall description of the IT spectra from the Cu(I)–M(III) centers, although a few significant details are not adequately explained. The spectra from the crystal contaiing Cu(I) and Cr(III) present a number of difficulties. Two bands appear in the 19 000- to 25 000-cm^{-1} region where only one IT transition is predicted. The stronger band at 22 800 cm^{-1} has a relatively small but clearly noticeable intensity in the perpendicular spectrum ($I_\parallel/I_\perp \sim 5$). It is possible that this band does not result from an IT transition of the Cu(I)–Cr(III) center; however, we have no alternative explanation. Other types of impurity centers as well as other oxidation states of copper and chromium may be present in the doped crystals. The spectra of $CsCdBr_3$ crystals doped with Cu(I) and Cr(III) exhibit the same partially polarized band ($I_\parallel/I_\perp \sim 3$) at approximately 23 000 cm^{-1}. The band at 28 500 cm^{-1} poses a problem in the sense that the calculated IT transition that compares most favorably in terms of energy is a two-electron excitation. It requires the promotion of one of the electrons on the Cr(III) ion as well as the transfer of an electron from the Cu(I) ion to produce a ${t_{2g}}^2{e_g}^2$ configuration. Two-electron transitions are usually forbidden. The 28 500-cm^{-1} band may actually correspond to the one-electron transition computed at 34 600 cm^{-1}. A somewhat more important feature that is unresolved in the theoretical analysis is the nature of the donor orbital in the copper(I) ion. It has been assumed that the transferred electron originates from the same copper(I) energy level in all of the IT transitions even though the octahedral ligand field must resolve the degeneracy of the Cu(I) d orbitals. Although there is no direct spectroscopic evidence it seems certain that ligand-field splitting between the t_{2g} and e_g sets of Cu(I) d orbitals is at least a few thousand cm^{-1}.

The electron-transfer processes of metal complexes, both optical and thermal, have been extensively studied and are still of great interest to chemists.[19] The IT absorptions of numerous inner-sphere and outer-sphere redox systems have been characterized by theoretical as well as experimental investigations. The Cu(I)–M(III) centers formed in the $CsMgCl_3$ crystals are unique in the sense that copper(I) may be combined with a number of different trivalent acceptor ions to give a series of redox complexes with nearly identical structures. It is very likely that there are other trivalent metals in addition to those used in this study that will form redox complexes with copper(I) in doped $CsMX_3$ crystals. The fact that, at low temperatures, the spectra are resolved well enough to distinguish different IT transitions is an important advantage of the $CsMgCl_3$/Cu(I)–M(III) system. The crystals are well suited for other spectroscopic techniques such as resonance Raman which could provide considerable additional information regarding the electron-transfer processes.

Registry No. $CsMgCl_3$, 13845-09-5; Cu, 7440-50-8; Cr(III), 16065-83-1; Mo(III), 22541-86-2; Ru(III), 22541-88-4; Rh(III), 16065-89-7.