^{55}Mn hyperfine coupling constants indicate that the extents of metal to ligand delocalization are approximately the same in the two host materials, for both V(II) and Mn(II). According to simple crystal field theory the *g* values of octahedral complexes containing d^3 or d^8 ions can be described by $g = 2 - 8\lambda/10Dq$.[25] Assuming that this expression is at least qualitatively correct, one would conclude that the ligand field splittings ($10Dq$) for Ni(II) and V(II) do not change significantly in going from $CsMgBr_3$ to $CsCdBr_3$. This conclusion is certainly supported by the similarity of the ligand field spectra of $CsNi_xMg_{1-x}Br_3$ and $CsNi_xCd_{1-x}Br_3$. It appears that the average distances between the impurity ion (V(II), Mn(II), or Ni(II)) and the six surrounding bromide ions are approximately the same in both host materials. Apparently the bromide ions in $CsMgBr_3$ and $CsCdBr_3$ are able to adjust their positions to match the size of a divalent impurity which is incorporated into the $[MBr_3^-]$ chains. One might describe these linear-chain salts as "accommodating" host lattices. This type of behavior is not generally typical of ionic host lattices. For example, it is quite evident from studies of V(II) crystals of $CsCdCl_3$[26] and $CsCaCl_3$[27] that the average metal–chlorine distances for the impurity ion are determined primarily by the host lattice. (Neither of these two host materials adopt the linear-chain $CsNiCl_3$ structure.)

It should be remembered that unlike the *g* values and hyperfine constants, the zero-field splittings of the three ions do differ significantly between $CsCdBr_3$ and $CsMgBr_3$. The zero-field splitting presumably reflects the trigonal distortion of a paramagnetic ion's environment. Thus, while the average metal–bromine distances for the three transition metal ions do not appear to change much from $CsCdBr_3$ to $CsMgBr_3$, the actual geometry of the $[MBr_6]^{4-}$ complex must vary significantly from one host material to the other.

Registry No. V(II), 15121-26-3; Mn(II), 16397-91-4; Ni(II), 14701-22-5; $CsCdBr_3$, 16593-55-8.

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Molecular *g* Values of the Planar $CuCl_4^{2-}$ Ion

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Because of the comparative simplicity of its electronic structure considerable theoretical interest has been shown in planar $CuCl_4^{2-}$, and several molecular orbital (MO) calculations[1-3] have been carried out on this ion. It has also been used as a model in the calculation of the EPR parameters[4,5] and electronic spectral transition energies[6] of metal complexes. The various MO calculations have suggested the orbital energy sequences $b_{1g}(d_{x^2-y^2}) >> a_{1g}(d_{z^2}) > e_g(d_{xz}, d_{yz}) > b_{2g}(d_{xy})$[2,3] and $b_{1g}(d_{x^2-y^2}) >> b_{2g}(d_{xy}) > e_g(d_{xz}, d_{yz}) > a_{1g}(d_{z^2})$,[1] while the orbital scheme $b_{1g}(d_{x^2-y^2}) >> b_{2g}(d_{xy}) > a_{1g}(d_{z^2}) > e_g(d_{xz}, d_{yz})$ has also been proposed[7] in a general MO treatment of planar metal complexes (the symmetry labels refer to the D_{4h} point group with the *x* and *y* axes lying along the bond directions). The further suggestion has been made that, despite an orbital sequence placing d_{z^2}, d_{xz}, d_{yz}, and d_{xy} all comparatively close in energy, interelectron repulsion effects will give rise to a sequence of *state* energies $^2B_{2g}(d_{xy}) \sim {}^2A_{1g} >> {}^2E_g >> {}^2B_{1g}$. It is only recently that a compound containing a strictly planar $CuCl_4^{2-}$ ion has been prepared:[8] $(N\text{-mph})_2CuCl_4$ (*N*-mph = *N*-methylphenethylammonium). Other complexes of general type $[\text{cation}]_2CuCl_4$ of known structure contain either distorted tetrahedral anions or polymeric structures with long axial bonds joining planar $CuCl_4^{2-}$ groupings.[9] In order to elucidate the electronic properties of isolated planar $CuCl_4^{2-}$ we have studied the single-crystal electronic and EPR spectra of $(N\text{-mph})_2CuCl_4$. The low-temperature "d–d" polarized electronic spectrum of the complex shows three well-resolved peaks at 11 760, 13 700, and 16 100 cm^{-1}, with each peak showing remarkably well-resolved vibrational fine structure.[10] Initial measurements made on the (010) crystal face pointed tentatively to the state energy sequence $^2E_g > {}^2B_{2g} > {}^2A_{1g} >> {}^2B_{1g}$.[10] Subsequent measurements on other crystal faces, however, now suggest[11] rather strongly the sequence $^2A_{1g} > {}^2E_g > {}^2B_{2g} >> {}^2B_{1g}$.

To complement the electronic spectral data we have measured the EPR spectra of single crystals of $(N\text{-mph})_2CuCl_4$ at room temperature using a JEOL JES-P-10 EPR spectrometer operating at X-band frequency for rotations of the magnetic field in the (010), (001), and *bc** crystal planes. A sample of 1% Mn^{2+} in MgO was used to calibrate the spectra and the values of g^2 for various orientations of the magnetic field are listed in Table I. Treatment of the data by a method described previously[12] yields the molecular *g* values $g_x = 2.040$ (0.002), $g_y = 2.040$ (0.004), and $g_z = 2.221$ (0.004), where the figure in parentheses represents the possible error. Here *x* and *y* were defined along the shorter and longer Cu–Cl bond directions (224.8 and 228.1 pm[8]), respectively. Within experimental error, the **g** tensor thus has axial symmetry. The molecular *g* values of planar $CuCl_4^{2-}$ have been calculated by Smith[4] using expressions which include charge-transfer states and the ligand portion of the ground-state wave function. These expressions are of the form

$$\Delta g_{\parallel} = K_{\parallel}(\text{d-d})/E[B_{2g}(\text{d-d})] + K_{\parallel}(\text{ct})/E[B_{2g}(\text{ct})] \qquad (1)$$

$$\Delta g_{\perp} = K_{\perp}(\text{d-d})/E[E_g(\text{d-d})] + K_{\perp}(\text{ct})/E[E_g(\text{ct})] \qquad (2)$$

where $\Delta g_{\parallel}$ and $\Delta g_{\perp}$ represent the *g* shifts relative to the free-electron value parallel and perpendicular to the symmetry axis, $E[B_{2g}(\text{d–d})]$ etc. represent the energies of the appropriate excited d–d or charge transfer (ct) states, and the values of $K_{\parallel}$ and $K_{\perp}$ depend on the spin–orbit coupling constants of

Table I. Measured Values of g^2 for Rotations of the Magnetic Field in the (001), (010), and bc^* Crystal Planes of $(N\text{-mph})_2CuCl_4$

bc^* plane			(001) plane			(010) plane			
Angle,[a] deg	g^2		Angle,[a] deg	g^2		Angle,[a] deg	g^2	Angle,[a] deg	g^2
25	4.6135	4.2324	−10	4.5542	4.3040	−90	4.4241	−35	4.1779
40	4.6692	4.1714	0	4.4100		−85	4.3935	−30	4.1931
55	4.6539	4.1714	20	4.5346	4.2793	−80	4.3450	−20	4.2546
70	4.5786	4.2457	35	4.6139	4.1801	−54	4.1761	−10	4.3267
90	4.4121		50	4.6315	4.1564	−51.5	4.1671	−5	4.3657
−70	4.5539	4.2546	65	4.5789	4.2062	−35.5	4.1715	0	4.4146
			80	4.4836	4.3176	−10.5	4.3222	5	4.4501
			−80	4.5110	4.3266	79.5	4.5199	25	4.6263
			−70	4.5740	4.2525	85	4.4811	35	4.6756
						−90	4.4429	40	4.6925
						−85	4.3866	45	4.7028
						−80	4.3496	50	4.6977
						−75	4.2994	55	4.6874
						−65	4.2326	60	4.6705
						−55	4.1822	70	4.6077
						−50	4.1757	80	4.5354
						−45	4.1671	85	4.4764

[a] Measured from the [100] direction in the (001) and (010) planes and the c^* direction in the bc^* plane. In the (010) plane a positive sign indicates rotation towards the positive c axis.

Table II. Calculated g Shifts for Planar $CuCl_4^{2-}$

$E(^2B_{2g}$(d–d)), cm^{-1}	$\Delta g_\parallel$[a]	$E(^2E_g$(d–d)), cm^{-1}	$\Delta g_\perp$[a]
11 760	0.204 (0.016)	11 760	0.041 (0.006)
13 700	0.187 (0.016)	13 700	0.039 (0.006)
16 130	0.171 (0.016)	16 130	0.038 (0.006)
	0.219 (0.004) (exptl)		0.038 (0.003) (exptl)

[a] The possible error is given in parentheses; for the calculated values this is derived from the uncertainty in the charge-transfer state energies.

copper and chlorine as well as various MO coefficients and overlap integrals. The values of $K_\parallel$(d–d) = 1428.7 cm^{-1}, $K_\parallel$(ct) = 2473.5 cm^{-1}, $K_\perp$(d–d) = 132.3 cm^{-1}, and $K_\perp$(ct) = 877.8 cm^{-1} are obtained using the expressions and data in ref 4, which utilizes MO coefficients from the calculation of Ros and Schuit.[1] Equations 1 and 2 may be used to calculate the g shifts of the planar $CuCl_4^{2-}$ ion in $(N\text{-mph})_2CuCl_4$ for all possible assignments of the "d–d" spectrum of this complex, and the results are shown in Table II. Here, the energies of the charge-transfer states have been taken[4] as 30 000 ± 5000 cm^{-1} (it is the uncertainty in these energies which produces the uncertainty in the g shifts). It can be seen that the calculated shifts are in good agreement with experiment particularly if, as is suggested by the recent electronic spectral measurements,[11] the $^2B_{1g} \rightarrow {}^2B_{2g}$ transition is assigned to the peak at 11 760 cm^{-1}. In particular, the MO calculations which assign this transition to the highest energy peak[2,3,6] are rendered rather improbable. The g values of planar $CuCl_4^{2-}$ have also been estimated by Zentsov et al., who reported shifts of $\Delta g_\parallel = 0.215$ and $\Delta g_\perp = 0.049$, the former value being in good and the latter in rather poor agreement with experiment. However, as full particulars of the parameters used in this latter calculation were not given, any comparison with experiment is tentative.

It is interesting to compare the g values of the planar anion in $(N\text{-mph})_2CuCl_4$ with those observed for copper chloride complexes having different stereochemistries. The g shifts $\Delta g_\parallel = 0.274$ (0.009) and $\Delta g_\perp = 0.051$ (0.002) have been reported[13] for the tetragonally distorted octahedral complex in $(C_2H_5NH_3)_2CuCl_4$, and virtually identical values have been observed[13,14] for the similar grouping in $(CH_3NH_3)_2CuCl_4$. Single-crystal studies[14] assign the electronic spectral transition energies as $^2B_{1g} \rightarrow {}^2B_{2g}$ at 12 200 cm^{-1} and $^2B_{1g} \rightarrow {}^2E_g$ at 13 300 cm^{-1} in $(CH_3NH_3)_2CuCl_4$. Use of the standard expressions $\Delta g_\parallel = -8\lambda k_\parallel^2/E[^2B_{2g}(\text{d–d})]$ and $\Delta g_\perp = -2\lambda k_\perp^2/E[^2E_g(\text{d–d})]$ yields orbital reduction parameters $k_\parallel^2 = 0.504$ and $k_\perp^2 = 0.409$ for these complexes. These may be compared with the values $k_\parallel^2 = 0.413$ and $k_\perp^2 = 0.326$ for the planar ion in $(N\text{-mph})_2CuCl_4$ assuming the preferred assignment of the electronic spectrum described previously. While it is true that orbital reduction parameters are related to covalency in a rather complicated way, it seems established that a relationship does exist[15] and that, where similar complexes are compared, a general decrease in the orbital reduction parameters accompanies an increase in covalency. As the presence of long axial bonds will have little effect on the g values,[4] the fact that $k_\parallel^2$ and $k_\perp^2$ decrease by a similar proportion on going from the distorted octahedral ligand arrangement in $(C_2H_5NH_3)_2CuCl_4$ to the planar anion in $(N\text{-mph})_2CuCl_4$ is consistent with the shortening of the Cu–Cl bonds (228.1[16] to 226.5 pm) which accompanies this change. The distorted tetrahedral anion in Cs_2CuCl_4 (Cu–Cl = 223.0 pm, ClCuCl = 129.2°[17]) has g shifts $\Delta g_\parallel = 0.382$ (0.006) and $\Delta g = 0.092$ (0.006)[16] and substitution of the relevant excited-state energies (7900 and 5175 cm^{-1}, respectively[18]) yields the orbital reduction parameters $k_\parallel^2 = 0.455$ and $k_\perp^2 = 0.284$. On going from a planar to a distorted tetrahedral geometry, the covalent interaction with the d_{xy} and $d_{x^2-y^2}$ should decrease, while that with the d_{xz} and d_{yz} orbitals should increase, which is quite consistent with the fact that on going from $(N\text{-mph})_2CuCl_4$ to $CsCuCl_4$ $k_\parallel^2$ is observed to increase and $k_\perp^2$ to decrease. Finally, it may be noted that the g shifts observed for Cu^{2+} doped into K_2PdCl_4,[19] $\Delta g_\parallel = 0.2303$ (2) and $\Delta g_\perp = 0.047$ (2), lie between those in the planar ion present in $(N\text{-mph})_2CuCl_4$ and the distorted octahedral grouping in $(C_2H_5NH_3)_2CuCl_4$; possibly the neighboring palladium ions (situated ~400 pm above and below each metal ion in K_2PdCl_4[20]) have a small influence on the electronic structure of the $CuCl_4^{2-}$ guest ion.

Registry No. $(N\text{-mph})_2CuCl_4$, 51751-77-0.

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Stoichiometry and Kinetics of the Cobalt(III) Oxidation of L-Ascorbic Acid in Acid Perchlorate Solution

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In recent years a considerable amount of kinetic data has been accumulated for redox reactions of aquocobalt(III) species.[2,3] These results are of interest in view of the strongly oxidizing character of the cobalt(III)/cobalt(II) couple ($E°$ = 1.86 V at $[HClO_4]$ = 3 M, 23 °C),[4] which evidently gives rise to limiting mechanisms for both inner- and outer-sphere aquocobalt(III) reactions.[5,6]

The rates of reduction of aquocobalt(III) species are characteristically first order in $[Co^{III}]$ and [reductant] and the second-order rate constant generally obeys the empirical relationship $k_{obsd} = a + b/[H^+]$. The parameters a and b are associated with reactions of Co^{3+}(aq) and $CoOH^{2+}$(aq), respectively.[3,6] Consideration of the values of kinetic parameters a and b for complexation and redox reactions indicates that the rates of reactions of $CoOH^{2+}$ with such reductants as Br^-, H_2O_2, and oxalic acid are limited by substitution of the reductant at the metal center with $a << b$,[5] while those of both cobalt(III) species with Fe^{2+},[7] benzenediols,[2,8] and I^- [2] are much faster and must therefore proceed through an outer-sphere mechanism. Another interesting feature of this latter class of reactions is the increasing importance of a relative to b in the empirical rate law.[5]

L-Ascorbic acid (I) plays an important reductive role in biochemical systems. This molecule has a stable enediol structure[9] and is oxidized by many transition metal centers to dehydroascorbic acid (II) (eq 1), a process which is formally analogous to the oxidation of benzenediols to the corresponding quinones.[2,8] Since a considerable amount of kinetic data has been accumulated for oxidation by aquocobalt(III) in these latter systems,[2,8] it seemed worthwhile to investigate the kinetic validity of this analogy for L-ascorbic acid oxidation.

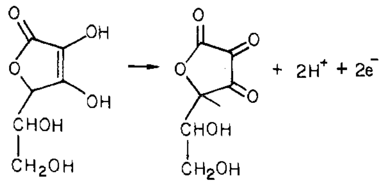
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Table I. Kinetic Data for Reduction of Aquocobalt(III) Species by Ascorbic Acid (Asc) at Ionic Strength 3.0 M

Temp, °C	$[H^+]$[a]	10^3[Asc][a]	k_{obsd}[b]	k_{calcd}[b,c]
5.0	3.0	4.12	1.36	1.22
		7.39	2.20	2.18
		14.7	3.91	4.34
	2.0	4.11	1.65	1.66
		7.38	2.96	2.98
		14.7	5.26	5.94
	1.0	4.25	3.31	3.10
		7.41	5.71	5.41
		14.15	10.1	10.3
	0.60	4.14	4.93	4.82
		7.39	8.13	8.61
		14.76	16.7	17.1
15.0	3.0	4.11	2.72	2.85
		7.34	5.37	5.10
		14.7	10.6	10.2
	2.0	4.50	4.50	4.21
		7.42	7.57	6.94
		14.73	14.7	13.8
	1.0	7.45	13.0	12.4
		13.34	23.2	22.1
	0.6	4.15	10.4	10.9
		7.36	20.5	19.3
		14.7	40.1	38.6
25.0	3.0	5.14[d]	8.02	8.00
		10.2	16.1	15.9
		10.2[d]	15.4	15.9
		15.3	26.0	23.8
		39.4[d]	58.3	61.3
	2.0	4.13	8.46	8.52
		7.20	15.8	14.9
		7.42	15.4	15.2
		14.5[d]	30.0	29.4
		14.7	29.2	30.4
		19.3	37.4	39.8
		23.2	44.5	47.9
		29.6	56.0	61.2
	1.0	3.92	18.7	14.1
		15.3[d]	59.8	54.9
	0.6	3.47	17.5	19.5
		4.42	23.5	24.8
		5.84	30.9	32.8

[a] All concentrations are M. $[Co^{III}]_0 = (8.43–23.2) \times 10^{-4}$ M; $[Co^{II}] = (1.36–5.25) \times 10^{-3}$ M. [b] Units are s^{-1}. Average error of repeated runs is ca. ±5%. [c] Calculated from eq 3 using the data in Table II. The data were weighted proportional to $(1/k_{obsd})^2$. [d] Alternate independent source of ascorbic acid.

In this paper we report a stopped-flow spectrophotometric determination of the rate law for the rapid oxidation of L-ascorbic acid by aquocobalt(III) species in aqueous perchloric acid at ionic strength 3 M.

Experimental Section

Materials and Analytical Methods. All water used in this investigation was either doubly distilled or distilled and then deionized. Stock solutions of approximately 6 M sodium perchlorate were prepared by neutralizing sodium carbonate with perchloric acid and were standardized gravimetrically. Cobalt(II) perchlorate hexahydrate was used to prepare the stock solutions of cobalt(III),[3] which were analyzed spectrophotometrically (ϵ_{605} 35.3 M^{-1} cm^{-1} and ϵ_{509} 4.84 M^{-1} cm^{-1}, respectively[2]). L-Ascorbic acid (different samples from Eastman) was used as supplied to make up stock aqueous solutions which were used within 1 h of preparation. Ascorbic acid concentrations were determined by coulometric titration with iodine.[10]

Stoichiometry Measurements. The stoichiometry of the oxidation reaction was determined by adding aliquots of a standardized solution of Co^{III} to excess analyzed ascorbic acid, neutralizing the excess perchloric acid with standard sodium hydroxide, and then determining the amount of unreacted ascorbic acid as described above in a solution