less than for the former. Similar linear correlations have been observed previously for d-block transition-metal couples containing substitutionally inert ammine ligands.[14,15] They arise from the more electropositive oxidized form of the redox couple being stabilized to a greater extent by solvent donor interactions than the reduced form.[14] Similar results were obtained for the corresponding Yb(III/II) and Sm(III/II) couples; the data for all these systems are summarized in Table II as "donor selectivities",[15] $[-\mathrm{d}E_f/\mathrm{d}(\mathrm{DN})]$.

The simplest interpretation of these data, expressed as a decrease in either $(-\mathrm{d}E_f/\mathrm{d}(\mathrm{DN})$ or $[\mathrm{d}E_f(\text{M–cryptand})/\mathrm{d}E_f(\text{M–solvento})]$ (Table II), is that the number of directly coordinated solvent molecules is about threefold smaller for the metal cryptates than for the nonencrypted cations. This presumes that the donor selectivity is proportional to the number of such "inner shell" solvent molecules. Evidence for a related effect has been obtained for mixed polypyridine–ammine couples, where the donor selectivity increases linearly with the number of ammine ligands.[15] Although these latter couples are coordinatively saturated and substitutionally inert, the solvent can interact specifically with the polar ammine ligands. Note that the cryptand ligands, like the polypyridines, contain no polar sites suitable for specific solute–solvent interactions. The number of inner-shell water molecules, *n*, coordinated to Eu(III) in aqueous media has been determined to be 8.3 ± 0.2 from X-ray diffraction data[16] and estimated to be about 9 on the basis of luminescence decay measurements.[8a,17] The latter method applied to $\mathrm{Eu(2.2.1)^{3+}}$ yielded $n = 3.2$.[6b] The present results are nicely consistent with this latter finding since they indicate that both the (2.2.1) and (2.2.2) cryptates allow about one-third as many solvent molecules to coordinate to the lanthanide cation as obtained in the absence of such solvent shielding. This finding is consistent with structural considerations in that the macrobicyclic structure of these cryptates leaves three gaps between the polyether strands with which solvent coordination to the metal is sterically possible.[18] The conclusion that the (2.2.1) cryptate provides only fractional (ca. 60–80%) shielding of Eu(III) from direct coordination by water can therefore now be generalized on the basis of our electrochemical data to europium, ytterbium, and samarium complexes with (2.2.2) as well as (2.2.1) cryptands and to several nonaqueous solvents in addition to water.

It is also of interest to examine the effect of metal encryptation on the reaction entropies, especially in view of our recent assessment of solvent and ligand effects upon $\Delta S_{\mathrm{rc}}^\circ$ for simple octahedral redox couples.[19] (The reaction entropy equals the difference of ionic entropies between the reduced and oxidized forms of the redox couple.) Inspection of the $\Delta S_{\mathrm{rc}}^\circ$ values for the Eu(III/II) couples in Table I shows that while they tend to be smaller for the cryptate compared with the solvento couples, the extent of this decrease is strongly dependent on the particular solvent. In addition, plots of $\Delta S_{\mathrm{rc}}^\circ$ against the solvent acceptor number, AN (Table I), found previously to be linear for a number of octahedral redox couples,[19] are markedly nonlinear for the present systems. Very similar solvent-dependent $\Delta S_{\mathrm{rc}}^\circ$ values were also obtained for the Yb(III/II) and Sm(III/II) couples. Especially discrepant in this regard are the relatively large $\Delta S_{\mathrm{rc}}^\circ$ values observed for the Eu(III/II) cryptates and especially $\mathrm{Eu^{3+/2+}}$ in water, in constrast to the small values expected on the basis of the $\Delta S_{\mathrm{rc}}^\circ$–AN correlation in ref 19. This has been noted previously for other aquo couples and ascribed to the influence of specific aquo ligand–solvent effects.[19]

This more complex influence of encryptation upon the reaction entropies and the absence of straightforward solvent shielding effects are almost undoubtedly due to the preponderant effect of solvent–solvent, and longer range ion–solvent, interactions upon the ionic entropies.[19] The solvent-dependent formal potentials (i.e., the ionic free energies), on the other hand, appear to be influenced primarily by short-range charge–solvent interactions so that the simple manifestation of solvent shielding upon encryptation with regard to this latter parameter is readily understandable.

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Registry No. DMF, 68-12-2; NMF, 123-39-7; $\mathrm{Me_2SO}$, 67-68-5; acetonitrile, 75-05-8; propylene carbonate, 2453-03-4; formamide, 75-12-7.

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Magnetic Susceptibility of Paraquat Hexabromodicuprate(II): Comparison of the Magnetochemistry of Copper(II) Chloride and Copper(II) Bromide Salts

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In the past decade, the magnetic properties of a large number of copper(II) halide salts have been investigated.[1,2] These include symmetrical bibridged systems,[3] asymmetrical bibridged systems,[4] tribridged systems,[5] and asymmetrical monobridged systems.[5] In examining these results when $|J/k|$ is relatively large ($|J/k| \geq 10$ K; $\mathcal{H} = -2J\mathbf{S}_1\cdot\mathbf{S}_2$), a number of systematics are apparent. First, it is observed that if the exchange interaction is ferromagnetic, the magnitude of the coupling is nearly the same for the bromide and chloride salts. However, if the coupling is antiferromagnetic, the magnitude for the bromide salts is several times larger than for the chlorides. Second, in systems where the spin anisotropy is known, the two types of salts have opposite anisotropies; e.g., if the chloride has a small Ising anisotropy, the bromide will have a *xy* anisotropy and vice versa.

In this paper a magnetic susceptibility study of (paraquat)$\mathrm{Cu_2Br_6}$ is reported, and the results are compared with those for the corresponding chloride salt. Next, the results of a reinvestigation of the magnetic susceptibilities of $\mathrm{CuCl_2}$ and $\mathrm{CuBr_2}$ are given. Finally, the role that the excitation energies for the ligand-to-metal charge-transfer states and the magnitude of the ligand spin–orbit coupling play in determining the behavior indicated above are discussed.

Experimental Section

(paraquat)$\mathrm{Cu_2Br_6}$ was prepared, following the procedure used for the corresponding chloride salts,[6] by dissolving stoichiometric amounts of paraquat and $\mathrm{CuBr_2}$ in a moderately dilute aqueous HBr solution and crystallizing by slow evaporation at room temperature.

Magnetic measurements on $\mathrm{CuBr_2}$ and (paraquat)$\mathrm{Cu_2Br_6}$ in the temperature range 78–300 K were performed at Washington State University on a PAR vibrating-sample magnetometer.[7] Measurements on

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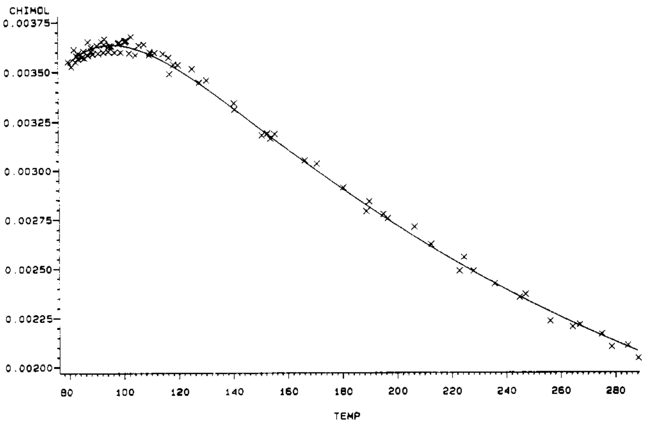

Figure 1. Plot of χ_m vs. T for (paraquat)Cu_2Br_6. Solid curve is for alternating chain model with $J/k = -74$ K and $\alpha = 0.23$ ($J'/k = -17$ K).

Table I. Magnetic Exchange Parameters for Symmetric Bibridged Copper(II) Halide Salts

	J/k, K		
compd	chloride	bromide	ref
CuX_2	−54	−165	*k*
$KCuX_3$	−28	−95	*a, b*
(paraquat)Cu_2X_6	−18	−74	*c, k*
$(CH_3)_2CHNH_3CuX_3$	−14	−90	*d, e*
$(CH_3)_2NH_2CuX_3$	15	−60	*c, f*
Ph_4PCuX_3	55	37	*g*
Ph_4AsCuX_3	28	28	*h, g*
$(C_6H_{11}NH_3)CuX_3$	50	50	*i, j*

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$CuCl_2$ were carried out at Iowa State University on a mutual inductance ac bridge in the range 2–300 K.[8]

The magnetic susceptibility of (paraquat)Cu_2Br_6 reaches a maximum at 94 K (Figure 1). From the persumed isomorphism of the structure with the corresponding chloride,[6] an alternating bibridged chain structure is anticipated. Symmetrical bridges exist within the $Cu_2Br_6^{2-}$ dimers; asymmetrical bridges exist between dimers. The temperature at the maximum uniquely fixes the strongest antiferromagnetic coupling at −75 K since the susceptibility of the antiferromagnetic chain in the dimer limit reaches a maximum at $T_{max} = 1.25|J/k|$. A least-squares fit to the alternating-chain model yields $J/k = -74$ K and $J'/k = -17$ K. It is known that the exchange coupling associated with asymmetrical bridges is invariably weak. Thus, it can be assumed that the larger J corresponds to the intradimer exchange ($J/k = -74$ K) and the smaller to the interdimer coupling ($J'/k = -17$ K).

The magnetic susceptibility data for $CuCl_2$ and $CuBr_2$ are characteristic of uniform antiferromagnetic chains. Our results are in agreement with those presented by Adams et al.[10] except that the position of the maxima in χ, especially for the chloride, is more cearly defined. Again, the temperature at which χ is a maximum determines J since $T_{max} = 1.3|J/k|$ for the uniform chain. For $CuCl_2$, χ_{max} occurs at $T = 70$ K so that $J/k = -54$ K while for $CuBr_2$, χ_{max} occurs at $T = 215$ K, which yields $J/k = -165$ K.

Exchange-Coupling Trends

In Table I, the observed magnetic exchange parameters are listed for a series of symmetrically bibridged copper(II) chloride and bromide salts. It is seen that, for most ferromagnetic salts in the series, the magnitude of J/k is approximately the same irrespective of the ligand. Similar results are observed for the asymmetric monobridged coupling in the ferromagnetic $(RNH_3)_2CuX_4$ systems. However, as the salts become antiferromagnetic, J/k decreases much more rapidly for the bromide salts than for the chloride salts. For those salts where structures are known for both the chloride and bromide analogues, little difference in the structures occur, other than those attributable to the larger ionic radius of the bromide ion. Thus, these trends cannot be accounted for by structural arguments. The cause can be readily seen, however, by examining the factors that affect the antiferromagnetic contribution to the exchange. In the Hoffmann formalism,[11] the exchange is expressed as

$$2J = 2J_F - \frac{(\epsilon_s - \epsilon_a)^2}{J_{aa} - J_{ab}}$$

Here J_{aa} and J_{ab} are one- and two-center Coulomb integrals, while ϵ_s and ϵ_a are the one-electron energies of the symmetric and antisymmetric combination of magnetic orbitals on the two metal centers. Thus, the exchange is ferromagnetic when $\epsilon_s \approx \epsilon_a$, and the antiferromagnetic contribution to the exchange goes as $(\epsilon_s - \epsilon_a)^2$. Hay et al. argue that $\epsilon_s - \epsilon_a$ is inversely proportional to the difference in energies between the ligand orbitals and the magnetic orbital on the metal. This quantity may be estimated from the intense ligand-to-metal charge-transfer transitions, which occur at the UV-visible borderline for the chloride salts (~25 000–30 000 cm^{-1}) but are in the middle of the visible region for the bromide salts (~15 000–20 000 cm^{-1}). Thus, it is expected that the antiferromagnetic contribution to the exchange, J_{AF}, will be 2–3 times larger for the bromide salts than for the chloride salts. This is in excellent agreement with the experimental trends, as can be seen in Figure 2 where J(Cl) is plotted vs. J(Br). A rough linear relationship is readily observed, with a slope of approximately $^1/_2$.

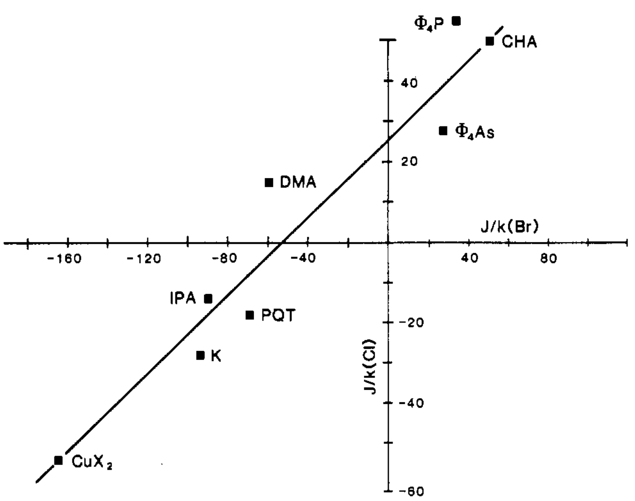

Figure 2. Plot of magnetic exchange constants for several copper(II) chloride salts, J/k(Cl), vs. exchange constants for the corresponding bromide salt, J/k(Br).

Spin Anisotropies

Copper(II) magnetic systems are essentially Heisenberg in nature. Small Ising or *xy* anisotropies are observed, however, usually on the order of 1–5%. While the anisotropies have been determined for several salts, only a few chloride/bromide pairs have been investigated. In the $(RNH_3)_2CuX_4$ system, the chloride salts normally have an *xy* type anisotropy[11] while the bromide analogues are more Ising-like.[12] The reverse is true for the system $(C_6H_{11}NH_3)CuX_3$.[13,14] These spin anisotropies are related to the

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anisotropic manner in which the spin–orbit coupling ties the spin to the lattice by mixing in orbital angular momentum to the spin system. This is manifest, for example (vide infra), in the anisotropy of the EPR **g** tensor. For elongated tetragonal or square-pyramidal environments, $g_\parallel > g_\perp$. In the chloride salts it is generally found that the magnetic easy axis (the preferred direction of spin orientation) is parallel to $g_\parallel$. This is reasonable since the magnetic energy decreases most rapidly when the field (external or internal) is along this direction. In systems where the **g** tensors of the copper ions are parallel (or nearly so), the chloride salts will have an axial (Ising) anisotropy. In contrast, in the $(RNH_3)_2CuCl_4$ systems, the local **g** tensors are perpendicular to each other and an easy plane (*xy*) type system is found.

The particular question now is why this same argument does not hold for the bromide salts. It is proposed that the answer lies with the nature of the spin–orbit coupling, particularly the role played by the ligand spin–orbit coupling. EPR studies have shown that the unpaired electron in square-planar CuX_4^{2-} salts is substantially (~50%) delocalized out onto the ligands.[15] Thus, the effective spin–orbit coupling parameter for these systems is

$$\lambda(CuX_4^{2-}) \approx \tfrac{1}{2}\lambda(Cu^{2+}) + \tfrac{1}{2}\lambda(X)$$

Now $\lambda(Cu^{2+}) = -830$ cm^{-1}, $\lambda(Cl^-) = +600$ cm^{-1} and $\lambda(Br^-) = +1560$ cm^{-1} so that, for the chloride salts, $\lambda(CuCl_4^{2-}) < 0$ while, for the bromide salts, $\lambda(CuBr_4^{2-}) > 0$. Thus, the effective coupling of the spin to the lattice changes sign and the anisotropies of the systems reverse when bromide is replaced by chloride.

It should be noted that these exchange anisotropies are of the same order of magnitude as dipolar energies. The latter then will influence the actual observed anisotropies, causing deviation from these simple predictions.

Conclusion

The magnetic properties of copper(II) halide salts are influenced greatly by the chemistry of the halide ion. The existance of lower lying charge-transfer states in the bromide salts enhances the antiferromagnetic contribution to the exchange as compared to the chloride salts. The ligand spin–orbit coupling influences the spin ansotropy of the systems. Previously we have also shown that these two factors affect both the EPR *g* values[15] and line widths.[16] Thus, despite their similar structural characteristics, the magnetic behavior of copper(II) chloride and bromide salts are greatly modified by variations in the electronic structure of the halide ions.

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