tube 0.763 g of this complex was added to 1.00 ml of water at 0°. At timed intervals 0.100-ml samples were taken and about 5% of the water was distilled and collected under vacuum. This water was converted to CO_2. The reaction of the dioxy complex with water to give the oxyhydroxy complex and OH^- is essentially complete and places the $[OH^-]$ at greater than 1.5 *M*.

C. To 25 ml of water containing 0.05 g of KCN at 0° was added 1.0 g of $K_3[Mo(O)(OH)(CN)_4]$ (^{18}O enriched). At timed intervals 5-ml samples were treated with 0.5 ml of a saturated $[Cr(en)_3]Cl_3$ solution at 0° and seeded, and the green crystals of $[Cr(en)_3][Mo(O)(OH)(CN)_4]\cdot H_2O$ were collected, washed with normal water and acetone, and dried under vacuum at room temperature for 12 hr. The salt was then converted to CO_2.

D. This was experimentally similar to procedure C but no cyanide ion was present.

The solid complexes and water samples were converted to pure CO_2 for isotopic measurement by heating in a sealed tube with a mixture of $HgCl_2$ and $Hg(CN)_2$ followed by purification of the gases volatile at −78° by preparative vapor-phase chromatography over silicon oil on firebrick. All operations have previously been shown not to induce exchange. Isotopic analysis was carried out on a Nuclide RMS instrument utilizing the 46/(45 + 44) ratio (R_N). A value of 4.00 × 10^{-3} was given a CO_2 standard and all reported ratios are normalized to it.

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Registry No. $[Mo(O)(OH)(CN)_4]^{3-}$, 52920-70-4; $[Mo(O)_2(CN)_4]^{4-}$, 52920-71-5.

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Magnetic Susceptibility of One-Dimensional Linear Chains of Ferromagnetically Coupled $Cu_2X_6^{2-}$ Dimers[1]

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The study of copper dimers with triplet ground states has been of much current interest.[3] In particular, it has been shown that the $Cu_2Cl_6^{2-}$ ion in $Ph_4AsCuCl_3$ existed with a triplet ground state with a singlet excited state at approximately 40 cm^{-1}.[4] The esr spectra of single crystals of the corresponding bromide salt and a mixed bromo–chloro salt are anomalous and suggest the possibility of interdimer interactions.[5] To investigate this possibility, as well as to determine the magnitude of the singlet–triplet splitting, a susceptibility study of $Ph_4AsCuBr_3$ and $Ph_4AsCuBrCl_2$ was initiated.

Experimental Section

The compounds are prepared by the slow evaporation of an aqueous solution of equimolar amounts of Ph_4AsBr and $CuBr_2$ or $CuCl_2\cdot 2H_2O$. Crystal X-Ray analysis showed that the deep purple crystals of both compounds are isomorphous with the corresponding chlorides and gave no evidence of a supercell structure. Major constituent analyses were performed by Chemalytic, Inc., of Tempe, Ariz. *Anal.* Calcd for $Ph_4AsCuBr_3$: C, 41.73; H, 2.92; Cu, 9.25; Br, 34.70. Found: C, 41.73; H, 2.85; Cu, 9.06; Br, 34.40. Calcd for $Ph_4AsCuBrCl_2$: C, 44.61; H, 3.12; Cu, 10.63; Cl, 5.48; Br, 24.73. Found: C, 44.84; H, 3.22; Cu, 10.74; Cl, 5.64; Br, 24.84.

Table I. Molar Susceptibility

T, K	$10^4\chi_M$	*T*, K	$10^4\chi_M$	*T*, K	$10^4\chi_M$
		$Ph_4AsCuBr_3$		Ph	
4.17	2309	41.27	220	169.0	57.2
5.06	1909	46.66	219	180.7	53.1
6.22	1605	50.85	192	188.3	50.6
7.33	1364	57.33	167	201.4	48.3
7.84	1262	62.56	153	205.4	47.0
9.37	1088	67.98	140	219.4	44.2
12.10	866	72.68	127	236.6	40.1
13.62	752	77.88	118	246.0	38.2
16.20	636	80.66	114	260.0	35.9
18.43	560	121.2	85.0	267.1	35.3
23.08	456	130.2	76.6	274.5	34.4
26.91	382	138.9	71.7	295.3	32.1
31.85	314	150.0	64.4	319.0	24.7
36.75	270	160.6	60.6		
		$Ph_4AsCuBrCl_2$			
4.20	2505	23.59	465	126.0	76.3
5.84	1816	25.75	424	136.0	70.6
5.72	1852	29.03	363	148.3	64.9
6.39	1652	31.21	348	160.8	60.0
6.70	1580	34.23	313	167.6	57.0
7.57	1444	41.66	258	177.6	54.1
8.15	1341	44.95	235	186.3	50.5
9.67	1126	49.23	217	201.0	47.8
10.26	1060	53.45	200	211.8	44.8
11.37	955	58.47	181	228.5	41.0
12.41	880	62.59	168	236.4	39.7
13.85	805	66.62	156	246.3	37.9
15.35	738	70.97	145	256.8	36.5
16.08	675	76.41	131	265.5	35.2
16.85	660	79.98	123	270.8	34.1
18.28	606	84.11	117	283.6	32.0
19.65	563	117.7	82.2	291.0	31.4
21.56	508				

The Faraday technique[6] was used for magnetic susceptibility measurements in the temperature region from 78 to 300 K. Susceptibilities in the temperature range 4.2–78 K were measured utilizing the inital susceptibility technique.[7] In both cases, data were collected on polycrystalline samples obtained by grinding up single-crystal specimens. The data are tabulated in Table I.

Results

The crystal structure of $Ph_4AsCuCl_3$ contains isolated $Cu_2Cl_6^{2-}$ dimers, with dimers well separated by the Ph_4As^+ cations except along the *c* axis where the shortest Cl–Cl distance was 6.7 Å.[8] This had no apparent effect on the magnetic properties, which were readily interpreted in terms of an isolated dimer with a triplet ground state and a singlet excited state.[9] For $Ph_4AsCuBr_3$ and $Ph_4AsCuBrCl_2$, preliminary plots of $1/\chi$ *vs.* *T* indicated that a similar analysis might be valid. However, the plots of χT *vs.* *T*, shown in Figure 1, reveal more complex behavior in these cases. At high temperature, the plots extrapolate to Curie constants consistent with equal populations of the singlet and triplet levels ($C = {}^3/_4 C_{\text{triplet}}$). As the temperature is lowered, the apparent Curie constants increase as the systems depopulate into the lower energy triplet states. However, instead of extrapolating to the expected value, C_{triplet}, the apparent Curie constants start to drop rapidly below 20 K.

Two possible explanations for this behavior were explored. One involves the assumption that the ground state possesses a large zero field splitting with the $M_s = \pm 1$ levels lying an energy, *D*, above the $M_s = 0$ level. The appropriate Ham-

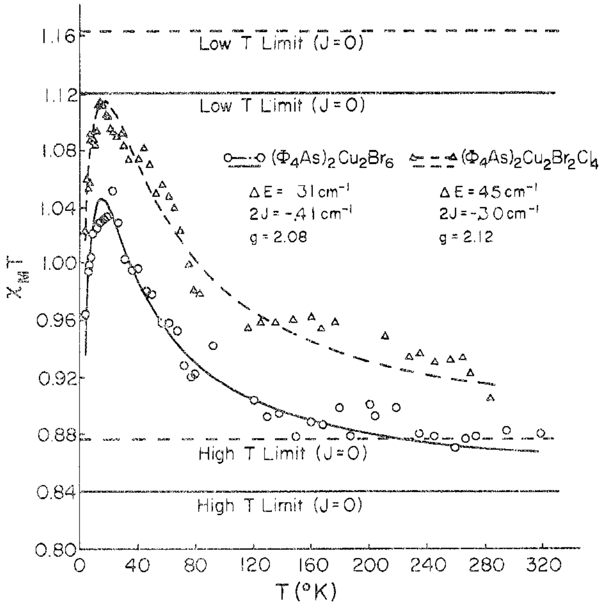

Figure 1. Plot of $\chi_M T$ *vs.* T, showing the experimental points (○) and theoretical curves (——) for $(Ph_4As)_2Cu_2Br_6$ as well as the experimental points (△) and theoretical curves (– – –) for $(Ph_4As)_2Cu_2Br_2Cl_4$. For each salt, the upper line corresponds to the expected value of $\chi_M T$ at $T = 0$ while the lower lines represent the expected values at $T = \infty$. The middle line in each case is the calculated curve for a linear chain of dimers (as defined in eq 1) for the values of the parameters listed.

iltonian for the system is then

$$H = (-\Delta E)S + D|M_s| + g\mu_\beta \vec{H}\cdot\vec{S}$$

and the susceptibility is given by

$$\chi_M = \frac{2Ng^2\mu_\beta^2}{3kT}\,\frac{3e^{-D/kT}}{1 + 2e^{-D/kT} + e^{-\Delta E/kT}}$$

Here, $\Delta E = -2J$ in the usual Heissenberg Hamiltonian, $H = -2Js_a \cdot s_b$; that is, a positive ΔE corresponds to a triplet ground state. The above notation allows one to write the Hamiltonian in terms of the spin quantum numbers of the dimer, rather than of the individual copper ions.

An excellent fit of the data is obtained with $D \approx 1.4$ cm⁻¹ and the singlet–triplet energy separation, ΔE, is 31 cm⁻¹ for $Ph_4AsCuBr_3$ and $D = 1.1$ cm⁻¹ and $\Delta E = 45$ cm⁻¹ for $Ph_4AsCuBrCl_2$. However, these values of D are an order of magnitude larger than that found in $Ph_4AsCuCl_3$.[10] There is no reason to suspect that it should be that much larger in these compounds. In addition, no X-band epr spectrum (except for the $m = \pm 2$ transition) would be expected for such a large zero-field splitting. Since a rich epr spectrum is observed, this cannot be the correct model for this system.

The second explanation involves the assumption that the larger size of the $Cu_2Br_6^{2-}$ and $Cu_2Br_2Cl_4^{2-}$ dimers, as compared to a $Cu_2Cl_6^{2-}$ dimer, brings the adjacent dimers along the *c* axis close enough together so that appreciable exchange coupling exists between dimers. Thus, the appropriate description of the system is that of a one-dimensional chain of copper dimers. In the Ising limit for the interdimer interactions, the Hamiltonian[11] is

$$H = -\Delta E \Sigma S_i - 2J'\Sigma M_s^{\,i} M_s^{\,i+1} + g\mu_\beta \Sigma \vec{H}\cdot\vec{S_i}$$

and the susceptibility is given by[7]

$$\chi_M = \frac{2Ng^2\mu_\beta^2\,[\alpha_1 e^{2\beta J'} - (e^{2\beta J'} - 1)(1 + e^{\beta\Delta E})]}{kTe^{-\beta\Delta E}(\alpha_1 - \alpha_2)(\alpha_1 - \alpha_3)} \qquad (1)$$

Table II. Singlet–Triplet Energy Separation (cm⁻¹) in Various $Cu_2X_6^{2-}$ Dimers

	X = Cl	X = Br
$KCuX_3$	–55	–195
$Me_2NH_2CuX_3$	~–5	–120
Ph_4AsCuX_3	40	31

where $\alpha_1 = a + b$, $\alpha_2 = a - b$, $\alpha_3 = 2e^{\beta\Delta E}\sinh(2\beta J)$

$$a = {}^1/_2\,[(1 + e^{\beta\Delta E}) + 2(\cosh(2\beta J'))e^{\beta\Delta E}]$$

$$b = {}^1/_2\,[1 + 10e^{\beta\Delta E} - 4(\cosh(2\beta J'))e^{\beta\Delta E} + 9e^{2\beta\Delta E} - 4(\cosh(2\beta J'))e^{2\beta\Delta E} + 4(\cosh^2(2\beta J'))e^{2\beta\Delta E}]^{1/2}$$

and $\beta = 1/kT$.

As can be seen from Figure 1, the model gives an excellent fit to the data. The interdimer coupling, 0.4 and 0.3 cm⁻¹, respectively, for the $Cu_2Br_6^{2-}$ and $Cu_2Br_2Cl_4^{2-}$ dimers, is very small, but its effect on the apparent Curie constant is quite marked. Since it is expected that the $Cu_2Br_6^{2-}$ dimer would be the larger of the two, the trend is in the correct direction. The singlet–triplet separation in both salts is comparable to that for $Ph_4AsCuCl_3$. Again, a reasonable trend is observed, with $\Delta E = 40$, 45, and 31 cm⁻¹ in the $CuCl_6^{2-}$, $Cu_2Br_2Cl_4^{2-}$, and $Cu_2Br_6^{2-}$ dimers, respectively.

Discussion

This study thus confirms the existence of a ground-state triplet in $Ph_4AsCuBr_3$, the first such case to be reported for a $Cu_2Br_6^{2-}$ dimer. Other $Cu_2Br_6^{2-}$ dimers have generally been strongly antiferromagnetically coupled; indeed, $CsCuBr_3$ is diamagnetic[12] (probably due to strong interdimer coupling, however) while the triplet state is 210 and 120 cm⁻¹ above the singlet ground state in $KCuBr_3$[13] and $(CH_3)_2NH_2CuBr_3$,[14] respectively.

Examination of Table II shows that the magnetic interactions in the bromide salt are more antiferromagnetic than in the corresponding chloride salts and that the range of singlet–triplet energy separations is larger. This can be explained on the basis of expected structural changes. It has been shown that the coupling in the chloride salts becomes more ferromagnetic as the bridging angle decreases due to the distortion of the $Cu_2Cl_6^{2-}$ ion from planarity.[4] While the corresponding bromide salts are isomorphous with the chloride salts, detailed structures are not known. Nevertheless, for the planar dimers ($KCuX_3$ salts), it is anticipated that the large Br^- ion will cause the Cu–Br–Cu angle to be larger than the Cu–Cl–Cu angle, thus making the interactions in $KCuBr_3$ more antiferromagnetic than in $KCuCl_3$. However, for the salts with tetrahedrally distorted coordination geometry around the Cu^{2+} ion ($Me_2NH_2CuX_3$ and Ph_4AsCuX_3), ligand–ligand repulsions will be greater in the bromide salts, thus giving a larger tetrahedral distortion. This will cause the Cu–Br–Cu angle to decrease more rapidly than the Cu–Cl–Cu angle, explaining the larger variation in singlet–triplet energy splittings observed in the bromide salts as compared to the chloride salts.

The fact that susceptibility data can be fit equally well by two physically different models has been noted previously.[15] It is thus necessary to make the selection of the best model based on other information (in this case, the epr data). Significantly, the singlet–triplet separation is insensitive to which model is used, which allows us to place confidence in the values of ΔE derived from the experimental data. This is not surprising, since ΔE is determined largely by the high-temperature (>20 K) portion of the data, while the effect of the interdimer coupling (or zero-field splitting) only manifests itself at the lower temperatures.

Intercluster interactions and their effect on magnetic properties have recently gained attention.[16] The superexchange pathways are not readily apparent in most cases. For the

Ph_4AsCuX_3 salts, the pathway is probably not a direct through-space interaction, the X–X distances between adjacent dimers being just too long. Rather, the interactions probably involve either the protons or the π system on the phenyl groups.

Ginsberg and Lines[16] have shown that, if the susceptibility of the cluster is given by

$$\chi_M = \frac{Ng^2\mu_\beta{}^2}{kT}F(J, T)$$

then interdimer interactions, J', can be accounted for, in a molecular field approximation, by the equation

$$\chi_M = \frac{Ng^2\mu_\beta{}^2}{k(T-\Theta)}F(J, T)$$

with $\Theta = 2J'z'(F(J, T))/k$, where z' is the number of nearest clusters. Thus Θ is (hopefully) only weakly temperature dependent. In the temperature regime $2J' \ll \Delta E \sim kT$, the susceptibility for a linear chain of dimers (eq 1) reduces to

$$\chi_M = \frac{Ng^2\mu_\beta{}^2}{k(T-\Theta)}\,\frac{e^{\Delta E/kT}}{1+3e^{\Delta E/kT}}$$

again with $\Delta E = 2J$. In this regime

$$\Theta = \frac{2J'}{k}\left[1 - \frac{1+e^{\Delta E/kT}}{1+3e^{\Delta E/kT}}\right] = \frac{2J'}{k}\left[\frac{2e^{\Delta E/kT}}{1+3e^{\Delta E/kT}}\right]$$

Thus, the results for the one-dimensional Ising model are identical with that of the molecular field approximation. For our system, $\Theta \approx {}^4/_3J'$. In $KCuBr_3$, whose structure consists of a linear chain of dimers, $\Theta = 17°$ was deduced from the susceptibility measurements.[13] This corresponds then to $2J' = 18\ cm^{-1}$.

It should be emphasized that the interdimer coupling could easily have missed if a plot of χT *vs.* T had not been made. While existence of triplet ground-state systems is relatively rare, if interdimer interactions are suspected, it is recommended that such plots be examined, since the effects discussed here will not be apparent on a $1/\chi$ *vs.* T plot.

Registry No. $(Ph_4As)_2Cu_2Br_6$, 52873-77-5; $(Ph_4As)_2Cu_2Br_2Cl_4$, 53154-28-2.

References and Notes

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Stable Intermediates in the Oxidative Degradation of Dodecahydrododecaborate(2−), $B_{12}H_{12}{}^{2-}$

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The unusual behavior of neutral or alkaline aqueous $KMnO_4$, which, unlike most stronger and weaker oxidizing agents, fails to yield coupled products but instead degrades the polyhedral ions $B_{10}H_{10}{}^{2-}$ and $B_{12}H_{12}{}^{2-}$ to boric acid, has been reported before.[1] The reaction with $B_{10}H_{10}{}^{2-}$ is so rapid that it has been used for a calorimetric determination of the reaction heat,[2] but $B_{12}H_{12}{}^{2-}$ reacts much slower so it appeared a logical reactant in our attempt to isolate the suspected reaction intermediates. Since hydroxylation is known to reduce the oxidative stability of the $B_{10}H_{10}{}^{2-}$ and $B_{12}H_{12}{}^{2-}$ ions,[3] a search for hydroxy derivatives appeared to be a reasonable first step in any attempt to elucidate the full mechanism of this interesting reaction. The results of this search are reported below.

Results and Discussion

The boric acid content of reaction mixtures with a progressively larger $MnO_4{}^-$:$B_{12}H_{12}{}^{2-}$ ratio was determined. The data shown in Table I reveal that except at very high ratios the yield of boric acid lags far behind the amount expected if no stable intermediates had been formed. Column 2 gives the maximum yield based on the stoichiometry of eq 1. Each

$$3B_{12}H_{12}{}^{2-} + 50MnO_4{}^- + 64H_2O = 36B(OH)_4{}^- + 50MnO_2 + 20OH^- \qquad (1)$$

experimental value in column 3 represents the average from three mixtures of same reagent ratio. The mixtures were made up with the two sets of solutions listed in the Experimental Section.

Three complete series of runs were made. In each series the amount of $B_{12}H_{12}{}^{2-}$ was maintained constant while that of $MnO_4{}^-$ was raised by dilution with a stock $MnO_4{}^-$ solution in fixed increments. Each increment was *equivalent* to the amount needed to substitute one hydroxy group in accordance with eq 2, and it may be referred to as "hydroxylation equivalent." Thus each series of runs began with a 2:3 and ended with a 50:3 molar reagent ratio. Though the only intermediates that we have been able to identify positively are $B_{12}H_{11}OH^{2-}$ and $B_{12}H_{10}(OH)_2{}^{2-}$, the progressive changes in the ir spectra and the tlc characteristics of the precipitated cesium salts leave little doubt that a number of more highly substituted ions are formed too.

$$3B_{12}H_{12}{}^{2-} + 2nMnO_4{}^- + nH_2O = 3B_{12}H_{12-n}(OH)_n{}^{2-} + 2nMnO_2 + 2nOH^- \qquad (2)$$

If the $MnO_4{}^-$ required for the observed boric acid formation according to eq 1 is subtracted from the total permanganate added and the remainder is assumed to have been used for hydroxylation according to eq 2, the average value of n shown in the fourth column of Table I can be obtained with the aid of a simple formula: $n_{av} = (n_0 - 25X_{BA})/(1 - X_{BA})$, where n_0 is the number of hydroxylation equivalents shown in the first column of Table I and X_{BA} is the fraction of $B_{12}H_{12}{}^{2-}$ converted to boric acid, computed from data in column 3. Examination of the last column of Table I reveals that as the yield of boric acid approaches the theoretical maximum, the average degree of hydroxylation falls steadily behind its