

impregnation of neutral clusters from solution. These results may have important implications for optimizing the turnover frequencies of clay-supported metal catalysts. Also, the surface selectivity of the reaction may be useful for estimating the edge surface area of layered silicates and for selectively decorating edge surfaces with heavy elements for studies of clay particle morphology by electron microscopy.

Acknowledgment. Partial support of this research by the National Science Foundation through Grant No. CHE-83-06583 is gratefully acknowledged.

Registry No. $\text{HO}_3(\text{CO})_{12}^+$, 47558-24-7; $\text{Os}_3(\text{CO})_{12}$, 15696-40-9; hectorite, 12173-47-6.

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Magnetic Circular Dichroism Spectra for Thallium(I), Lead(II), and Bismuth(III) Ions in Aqueous Acid Solution

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Received October 26, 1984

The metal ions of $6s^2$ electronic configuration, Tl(I), Pb(II), and Bi(III), in aqueous acid solution each exhibit an intense broad band in the UV region $4.2\text{--}5.2\ \mu\text{m}^{-1}$. These bands have been assigned as $6s^2 \rightarrow 6s6p$ metal-localized transitions primarily on the basis of their analogy to the intense UV absorptions observed for a variety of ns^2 ions doped into cubic alkali-metal halide lattices.¹ A considerable body of experimental data has been accumulated for these doped lattices,¹⁻⁵ including absorption, magnetic circular dichroism (MCD), and emission spectra, with some studies over a wide temperature range. The ns^2 ions are believed to occupy cubic sites, and the states of the excited $nsnp$ configuration that give rise to the UV bands (labeled A, B, and C in order to increasing energy) are designated $^3T_{1u}$ (allowed by spin-orbit coupling, intensity parallels ζ_{mp}), $^3E_u + ^3T_{2u}$ (weak, both states vibronic), and $^1T_{1u}$ (intense, allowed), respectively, in order of increasing energy.² These states correlate with 3P_1 , 3P_2 , and 1P_1 atomic states of the free ions. A $^3A_{1u}$ state correlating with 3P_0 is also predicted but not observed because it is strongly forbidden.

In contrast to the solid-state studies, the nature of the excited state(s) exhibited by the ions in solution is not well understood. In fact the structure of the solution species for the $6s^2$ ions in acid is not known for certain. The coordination number of Tl(I) is ill-defined, similar to that of an alkali-metal ion,⁶ and both Pb(II) and Bi(III) are known to form polynuclear hydroxo- or oxo-bridged clusters as the pH is raised. Thus $\text{Pb}_4(\text{OH})_4^{4+}$ and $\text{Pb}_6(\text{OH})_6^{6+}$ ions have been shown to crystallize from lead(II) perchlorate solutions,⁷ and the $\text{Bi}_6\text{O}_4(\text{OH})_4^{6+}$ ions have been identified in solution and in a solid perchlorate salt.⁸

- (1) See, for example: Jørgensen, C. K. "Absorption Spectra and Chemical Bonding in Complexes"; Addison-Wesley: Reading, MA, 1962; pp 185-189.
- (2) Tsuboi, T.; Stillman, M. J.; Jacobs, P. W. M. *Chem. Phys. Lett.* **1980**, *74*, 135.
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- (7) Hong, S.-H.; Olin, Å. *Acta Chem. Scand., Ser. A* **1974**, *A28*, 233. Olin, Å.; Soderquist, R. *Acta Chem. Scand.* **1972**, *26*, 3505. Johansson, G.; Olin, Å. *Acta Chem. Scand.* **1968**, *22*, 3197.
- (8) Sundvall, B. *Inorg. Chem.* **1983**, *22*, 1906; *Acta Chem. Scand., Ser. A* **1980**, *A34*, 93.

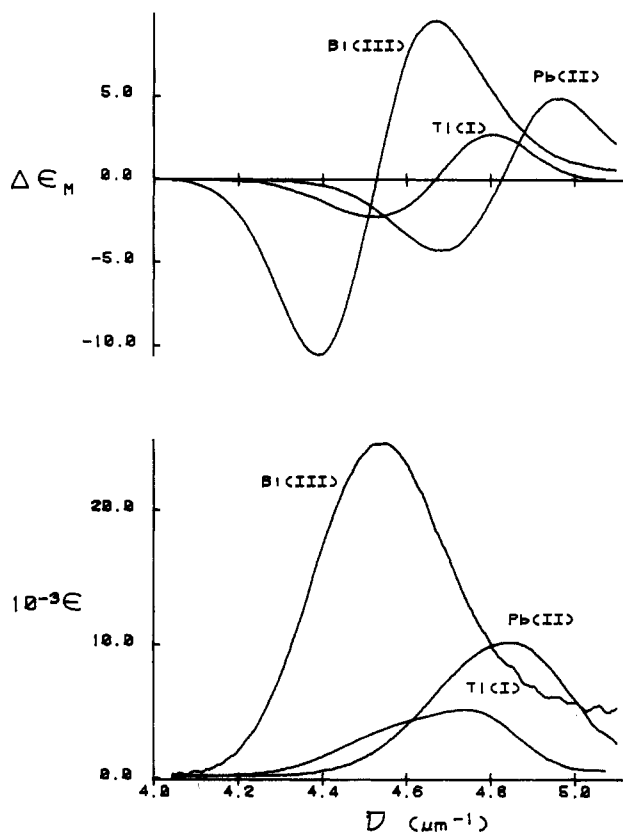


Figure 1. Electronic absorption (lower curves) and MCD (upper curves) spectra for Tl(I) in 0.100 M HClO_4 , Pb(II) in 0.100 M HClO_4 , and Bi(III) in 1.00 M HClO_4 .

Table I. Spectral Data

| λ_{max} , nm | absorption | | | MCD | | |
|-----------------------------------|----------------------------------|--|---------|----------------------------------|---|-------------------|
| | $\bar{\nu}$, μm^{-1} | ϵ , $\text{M}^{-1}\text{cm}^{-1}$ | D_0^a | $\bar{\nu}$, μm^{-1} | $\Delta\epsilon_M$, $(\text{M cm T})^{-1}$ | \bar{A}_1/D_0^a |
| Tl(I) in 0.100 M HClO_4 | | | | | | |
| 213 | 4.69 | 4860 | 1.4 | 4.48 | -2.24 | +1.9 ^b |
| | | | | 4.62 | 0 | |
| | | | | 4.76 | +2.76 | |
| Pb(II) in 0.100 M HClO_4 | | | | | | |
| 208 | 4.80 | 9890 | 2.0 | 4.63 | -4.25 | +2.1 ^c |
| | | | | 4.78 | 0 | |
| | | | | 4.91 | +4.95 | |
| Bi(III) in 1.00 M HClO_4 | | | | | | |
| 223 | 4.49 | 23800 | 5.4 | 4.35 | -10.5 | +1.9 ^d |
| | | | | 4.49 | 0 | |
| | | | | 4.63 | +9.6 | |

^a From a moment analysis of the data (see ref 9 for details). ^b $B_0/D_0 = -8 \times 10^{-3}/\text{cm}^{-1}$. ^c $B_0/D_0 = -5 \times 10^{-4}/\text{cm}^{-1}$. ^d $B_0/D_0 = -1 \times 10^{-4}/\text{cm}^{-1}$.

The purpose of this note is to report some MCD spectra⁹ for Tl(I), Pb(II), Bi(III) in perchloric acid solution. These spectra provide some additional spectroscopic information on which to base the assignment of the UV absorptions and hopefully provide some insight into the nature of the solution species and their excited states.

Experimental Section

Solutions of Tl(I) were prepared by dissolving thallium metal in HClO_4 and diluting to give 0.100 M HClO_4 ; solutions of Pb(II) were prepared by dissolving $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ in 0.100 M HClO_4 , and those

- (9) For a review of MCD spectroscopy, together with the standard conventions used here, see: Piepho, S. B.; Schatz, P. N. "Group Theory in Spectroscopy with Applications to Magnetic Circular Dichroism"; Wiley: New York, 1983.

of Bi(III) were prepared by dissolving $(\text{BiO})_2\text{CO}_3$ in 1.00 M HClO_4 . Absorption spectra were obtained by using a Cary 1501 spectrophotometer; absorption and MCD spectra at 7.0 T were determined simultaneously along the same light path by means of a computer-controlled spectrometer described elsewhere.¹⁰ The Tl(I) and Pb(II) solutions studied were 0.100 M in HClO_4 while the Bi(III) solutions were 1.00 M in HClO_4 , and the spectra were all corrected for the solvent blank.

Experimental MCD A_1 and B_0 parameters were determined from a moment analysis of the MCD spectra.⁹ The average energy about which the moments were determined, $\bar{\nu}_0$, was obtained by setting the first moment of the absorption to zero. A_1 parameters were evaluated from $\int (\Delta\epsilon_M/\bar{\nu})(\bar{\nu} - \bar{\nu}_0) d\bar{\nu} = (\Delta\epsilon_M)_1 = 152.5A_1$; B_0 parameters, from $\int (\Delta\epsilon_M/\bar{\nu}) d\bar{\nu} = (\Delta\epsilon_M)_0 = 152.5B_0$; and the values of D_0 (the dipole strength), from $\int (\epsilon/\bar{\nu}) d\bar{\nu} = \langle \epsilon \rangle_0 = 326.6D_0$. The quantity $\Delta\epsilon_M$ is the differential molar absorptivity per unit magnetic field with units $(\text{M cm T})^{-1}$.

Results and Discussion

Absorption and MCD spectra for Tl(I), Pb(II), and Bi(III) in dilute HClO_4 are presented in Figure 1, while quantitative spectral data and MCD parameters are collected in Table I. Beer's law was obeyed for the spectra of each metal ion in the range 10^{-4} – 10^{-5} M.

The prominent positive MCD A term observed for the UV band of each $6s^2$ ion¹¹ implies a degenerate excited state, or at least a nearly degenerate pair of states that couple in the magnetic field (pseudo- A term).⁹ In this respect the solution results are analogous to the lowest energy or A band for ns^2 ions in alkali-metal halide lattices, where a strong positive A term is also observed in all cases investigated by MCD.^{2,4,5} Since no weaker bands are found to lower energy for the $6s^2$ ions, the MCD thus supports the assignment of the solution bands, as in the solid, as due to the excitation to the spin-orbit state correlating with the 3P_1 atomic state of the $6s6p$ configuration. The symmetry of this spin-orbit state unfortunately cannot be specified precisely because the environment about each $6s^2$ ion is not known. However the similarity of the solution MCD among the three ions and with the solid-state work suggests that the symmetry is not drastically lower than cubic (O_h or T_d). If there were significant distortion from cubic, a splitting of the absorption band and a degradation of the A term would be expected due to the removal of the threefold degeneracy of the T_{1u} (O_h) or T_2 (T_d) spin-orbit state. A close inspection of the Tl(I) absorption band shows that it is unsymmetrical with a suggestion of a shoulder on the low-energy side of the maximum. The MCD A term however is quite symmetrical. The unsymmetrical absorption band may be an indication of a lower symmetry solution species for Tl(I), but to say more from the present results would be speculative. It may be remarked further that the MCD cannot differentiate in any simple way between O_h and T_d symmetries for the $6s6p$ transitions because the A terms predicted for both the T_{1u} (3P_1) and T_2 (3P_1) spin-orbit states are the same. Admitting ignorance of the actual symmetry of the spin-orbit state, the discussion that follows will refer simply to the atomic state 3P_1 , with which it correlates. In any event the metal-localized nature of the $6s6p$ transitions is not likely to be strongly altered by the environmental symmetry.

The assignment of the UV bands of the $6s^2$ ions to the 3P_1 spin-orbit state is further supported by the observation that the relative intensities of the absorption parallel the strength of spin-orbit coupling, which increases as $\text{Tl(I)} < \text{Pb(II)} < \text{Bi(III)}$ (ζ_{6p} values for the gaseous ions are 0.818, 1.239, and $1.699 \mu\text{m}^{-1}$, respectively).¹ This intensity pattern can be traced to increasing proportion of the allowed state correlating with the higher energy 1P_1 atomic state (corresponding to the C band in the solid-state studies). The spin-orbit states can be described as in eq 1 and 2, where $|A\rangle$ corresponds to the lower energy state of triplet

$$|A\rangle = -a|^1P_1\rangle + b|^3P_1\rangle \quad (1)$$

$$|C\rangle = b|^1P_1\rangle + a|^3P_1\rangle \quad (2)$$

parentage and $|C\rangle$ corresponds to the higher energy state, which is predominantly singlet; a and b are mixing coefficients such that

$b > a$ and $a^2 + b^2 = 1$. From this description of the $|A\rangle$ state, the MCD A -term ratio \bar{A}_1/\bar{D}_0 for isotropic molecules in solution⁹ can be calculated by eq 3, where the reduced matrix element

$$\bar{A}_1/\bar{D}_0 = (6^{1/2}/3)\langle A||L + 2S||A\rangle \quad (3)$$

contains the orbital and spin angular momentum operators. By combining eq 1 and 3, approximating the metal orbitals as pure $6s$ and $6p$ atomic orbitals, and evaluating the reduced matrix element, one obtains eq 4. The two contributions from the 3P_1

$$\bar{A}_1/\bar{D}_0 = 2|a|^2 + (1 + 2)|b|^2 \quad (4)$$

state (the coefficients of $|b|^2$ in eq 4) are due to its orbital and spin angular momentum. From eq 4 the limiting value of \bar{A}_1/\bar{D}_0 for the $|A\rangle$ state is +3 when $a \sim 0$ and $b \sim 1$. The values obtained from the experimental spectra (Table I) are +1.9, +2.1, and +1.9 for Tl(I), Pb(II), and Bi(III) respectively. They are all positive in agreement with prediction, but they indicate a 30–40% reduction in angular momentum in the $|A\rangle$ state. A similar reduction of angular momentum has been found from MCD studies of several ns^2 ions in alkali-metal halide lattices^{2,4,5} and also for some halo complexes of the $6s^2$ ions in solution.¹² Quenching of angular momentum appears to be a general characteristic of $nsnp$ excited states. Nearly complete quenching of the orbital component has been suggested.⁵ If the orbital contribution for the $|A\rangle$ state were ~ 0 , then the expected \bar{A}_1/\bar{D}_0 should be +2, in agreement with experiment for the $6s^2$ ions in solution. Orbital angular momentum can be reduced by (1) participation of the $6p$ orbitals in covalent bonding, (2) an excited state Jahn-Teller distortion, or (3) contributions to the $|A\rangle$ state from higher energy states with angular momentum of opposite sign, such as those arising from $5d^96p$ configurations. Although it is not possible from the present results to be precise, covalency is the most likely contribution to the quenching. Except for possibly Tl(I), excited-state distortions are small since no band splitting is observed, and the $5d^96p$ configurations contributions are expected to be small because of the large energy gap between the $5d^96p$ and $6s6p$ configurations (estimated from atomic spectral data¹³ for gaseous ions to be ca. 6, 9, and $15 \mu\text{m}^{-1}$ for Tl(I), Pb(II), and Bi(III), respectively). Significant covalent interaction involving the empty $6p$ orbitals is certainly anticipated when the $6s^2$ metal ions are surrounded by potential donor ligands as present in solution (H_2O molecules or OH^- ions, depending upon the pH).

Registry No. Tl(I), 22537-56-0; Pb(II), 14280-50-3; Bi(III), 23713-46-4.

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Preparation and Resolution of *cis*-Dicyanobis(ethylenediamine)chromium(III) Chloride

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Received August 19, 1984

Some mixed cyanochromium(III) complexes have not been adequately studied, leaving many important problems to be clarified with respect to their structures and properties, because the appropriate synthetic methods have not been known. The authors, being interested in these complexes,¹ recently elucidated the obscure properties of such optically active complexes by ac-

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(11) B term contributions were found to be quite small—see Table I.

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