of Bi(III) were prepared by dissolving $(BiO)_2CO_3$ 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 $\int(\Delta\epsilon_M/\bar{\nu})(\bar{\nu} - \bar{\nu}_0)\,d\bar{\nu} = \langle\Delta\epsilon_M\rangle_1 = 152.5A_1$; B_0 parameters, from $\int(\Delta\epsilon_M/\bar{\nu})\,d\bar{\nu} = \langle\Delta\epsilon_M\rangle_0 = 152.5B_0$; 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 $(M\ cm\ T)^{-1}$.

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 $6s^2$ ion[11] 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 Tl(I) < Pb(II), < Bi(III) (ζ_{6p} values for the gaseous ions are 0.818, 1.239, and 1.699 μm^{-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

$$|\mathrm{A}\rangle = -a|{}^1\mathrm{P}_1\rangle + b|{}^3\mathrm{P}_1\rangle \tag{1}$$

$$|\mathrm{C}\rangle = b|{}^1\mathrm{P}_1\rangle + a|{}^3\mathrm{P}_1\rangle \tag{2}$$

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 solution[9] can be calculated by eq 3, where the reduced matrix element

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

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 $^3P_1$

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

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 $\sim$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), exicted-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 data[13] for gaseous ions to be ca. 6, 9, and 15 μm^{-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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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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Table I. Optical Rotations (deg) Measured[a] at Wavelengths 589 and 546 nm

$[Cr(CN)_2(en)_2]C_{10}H_{14}SO_4Br$	$[Cr(CN)_2(en)_2]Cl$	$[Cr(CN)_2(en)_2]ClO_4$
$[\alpha]^{20}_{589} = +71.7$	$[\alpha]^{20}_{589} = +39.7$	$[\alpha]^{15}_{589} = +29.3$
$[M]^{20}_{589} = +383.2$	$[M]^{20}_{589} = +103.2$	$[M]^{15}_{589} = +94.8$
$[\alpha]^{20}_{546} = +98.1$	$[\alpha]^{20}_{546} = +73.5$	$[\alpha]^{15}_{546} = +54.3$
$[M]^{20}_{546} = +524.1$	$[M]^{20}_{546} = +190.8$	$[M]^{15}_{546} = +175.7$

[a] Reported values: for $[Cr(CN)_2(en)_2]C_{10}H_{14}SO_4Br$, $[\alpha]_{589} = +66.8°$,[2] $[\alpha]_{546} = +94.7°$,[2] and $[\alpha]_{589} = +71.5°$,[3] for $[Cr(CN)_2(en)_2]ClO_4$, $[M]_{546} = +19°$.[2]

complishing an effective new synthetic method.[2,3] In the present work, one such complex, *cis*-$[Cr(CN)_2(en)_2]Cl$, was synthesized in pure form and in good yield in a nonaqueous solvent. Thus, the complex chloride and perchlorate were resolved pure, and their optical properties were clarified.

Experimental Section

Synthesis of *cis*-Dicyanobis(ethylenediamine)chromium(III) Chloride. KCN (2 g) and $[Cr(en)_3]Cl_3 \cdot 3.5H_2O$ (5 g) were dissolved in 300 mL of warm (80 °C) absolute dimethyl sulfoxide, Me_2SO, to react for 1.5 h at 80 °C with stirring. The reaction mixture was diluted with water and passed through a Mg form cation-exchange resin (Dowex 50W-X4) column. The column, after it was washed with a water, was eluted with 1.0 M $MgCl_2$ solution. A yellow eluate was collected, and then a major portion of water was removed below 30 °C in a rotary evaporator. $MgCl_2$ crystals meanwhile deposited were removed by filtration. From the filtrate, yellow crystals were precipitated by adding ethanol and cooling and recrystallized from a minimum volume of water by the same treatment. The product, which proved to be *cis*-$[Cr(CN)_2(en)_2]Cl$, was collected by filtration, washed with ethanol, and dried under vacuum; yield 1.2 g (35%). Anal. Calcd for $[Cr(CN)_2(en)_2]Cl \cdot H_2O$: C, 25.95; H, 6.53; N, 30.26; Cl, 12.77; Cr, 18.72. Found: C, 26.16; H, 6.25; N, 30.46; Cl, 12.56; Cr, 18.91.

Resolution of the Dicyanobis(ethylenediamine)chromium(III) Chloride. To a solution of *cis*-$[Cr(CN)_2(en)_2]Cl \cdot H_2O$ (5 g, 0.018 mol) in 40 mL of water was added $(+)_{589}$-ammonium-3-bromo-*d*-camphor-8-sulfonate (3.1 g, 0.01 mol) in 20 mL of water, the solution being stirred rapidly 5 min. The yellow crystals that formed were filtered, washed with ethanol, and dried. Recrystallization was effected by dissolution in warm water (60 °C, 270 mL) and cooling; yield 2.4 g (48%). Anal. Calcd for $[Cr(CN)_2(en)_2]C_{10}H_{14}SO_4Br$: C, 35.96; H, 5.66; N, 15.75; Cr, 9.73. Found: C, 35.65; H, 5.65; N, 15.53; Cr, 9.48. The optically active chloride was obtained by the following procedure: An aqueous solution of the diastereomer (1.5 g) was charged on a Cl form anion-exchange resin (Amberlite IRA-400) column. The eluate from the column was evaporated to dryness below 30 °C and crystallized by the dissolution in water (10 mL) followed by the addition of ethanol and cooling; yield 1.2 g. Anal. Calcd for $(+)_{589}$-$[Cr(CN)_2(en)_2]Cl \cdot H_2O$: C, 25.95; H, 6.53; N, 30.26; Cl, 12.77; Cr, 18.72; H_2O, 6.5. Found: C, 26.29; H, 6.91; N, 30.10; Cl, 12.98; Cr, 18.66; H_2O, 6.0. Prolonged drying over KOH in a desiccator yielded the anhydrous complex. Anal. Calcd for $(+)_{589}$-$[Cr(CN)_2(en)_2]Cl$: C, 27.75; H, 6.21; N, 32.36; Cl, 13.65; Cr, 20.02. Found: C, 27.58; H, 6.33; N, 32.28; Cl, 13.50; Cr, 19.93.

The Perchlorate Complex. The aqueous solution of 1.5 g of the diastereomer was passed through the Cl form anion-exchange resin (Amberlite IRA-400) column. The eluate was condensed to about 10 mL, and 0.4 g of $NaClO_4$ was dissolved in it to precipitate granular yellow crystals, which were filtered and washed with ethanol. The product was recrystallized by addition of a small amount of $NaClO_4$ to the almost saturated aqueous solution; yield 0.5 g. Anal. Calcd for $(+)_{589}$-$[Cr(CN)_2(en)_2]ClO_4$: C, 22.26; H, 4.98; N, 25.96; Cr, 16.06. Found: C, 22.48; H, 5.20; N, 25.88; Cr 16.30.

Results and Discussion

In the past there was no appropriate method for synthesizing $[Cr(CN)_2(en)_2]Cl$ in a good yield. The methods previously used involved solely an aqueous solvent, which would inevitably degrade the desired complex by aquation since $[Cr(CN)_2(en)_2]^+$ aquates readily. Aquation is greatly accelerated by heating, so that heating cannot be used in an aqueous system. For example, the complex in an aqueous solution quickly turns into the hydrate when heated to 70 °C. The new method for the synthesis used Me_2SO[4] as the solvent, avoiding the aqueous solvent which is the principal cause of the degradation. By the new method, *cis*-$[Cr(CN)_2(en)_2]^+$ was easily obtained in a good yield.

$[Cr(en)_3]Cl_3$ reacted with KCN in warm Me_2SO, a solvent that could adequately dissolve the starting materials, substituting one of the three ethylenediamine ligands by two cyanide ions. After the reaction, Me_2SO and byproduct anion complexes can be separated by the cation-exchange resin from the desired cationic complex and unchanged $[Cr(en)_3]^{3+}$. Elution with 1 M $MgCl_2$ released the desired complex from unchanged $[Cr(en)_3]^{3+}$, which stayed at the same position of the column. Fractions containing the product were concentrated and precipitated with ethanol to yield the desired complex, which was insoluble in ethanol, whereas $MgCl_2$ is soluble.

Our synthetic method yielded only the cis form of the complex. The band of $[Cr(CN)_2(en)_2]Cl$ on a cellulose column did not separate into more than one band, despite the marked function of the cellulose column for separating this sort of structural isomers.[5] The complex contained in this band was confirmed to be *cis*-$[Cr(CN)_2(en)_2]Cl$ by the following observations: (1) The $[Cr(CN)_2(en)_2]Cl$ thus obtained formed a diastereomer with the optical resolution agent in 96% yield. (2) The positions and number of absorption bands in the IR range[6] (at 1606 and 1587 cm^{-1} due to NH_2 stretching and at 882 and 870 cm^{-1} due to NH_2 wagging) are consistent with cis form of the complex.

The optical rotation at wavelengths 589 and 546 nm, of diastereomer, chloride, and perchlorate salts are shown in Table I. The values previously reported are also shown. Among them, the molecular rotation for the perchlorate reported by Kaizaki et al.[2] (+19°) was very small in comparison with our value (+175.7°).

Registry No. *cis*-$[Cr(CN)_2(en)_2]Cl$, 58602-38-3; $[Cr(CN)_2(en)_2]C_{10}H_{14}SO_4Br$, 96290-32-3; $(+)_{589}$-$[Cr(CN)_2(en)_2]Cl$, 55659-59-1; $(+)_{589}$-$[Cr(CN)_2(en)_2]ClO_4$, 55659-58-0; $[Cr(en)_3]Cl_3$, 14023-00-8.

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