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THE SINGLE-CRYSTAL AND ION-ASSOCIATION CIRCULAR DICHROISM SPECTRA OF THE BIS[(R)-2-METHYL-1,4,7-TRIAZACYCLONONANE]COBALT(III) ION

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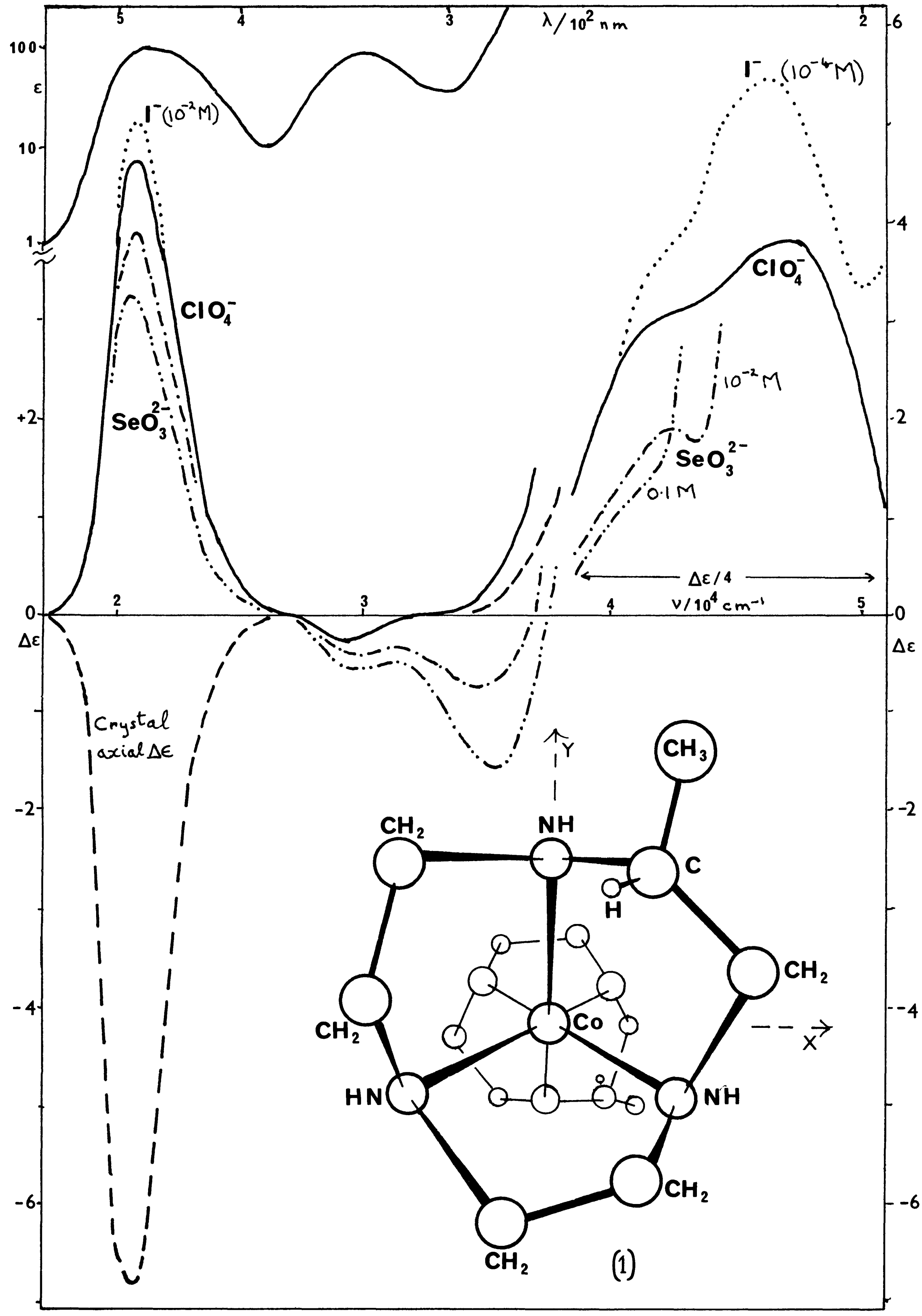
The CD spectrum of a single crystal of $[Co(R\text{-}MeTACN)_2]I_3.5H_2O$ and of an aqueous solution of the complex show, by comparison with the corresponding CD spectra of Λ-(+)-$[Co(en)_3]Cl_3$, that, of the two D_3 components of the transition to the octahedral $^1T_1$ state of the $[Co^{(III)}N_6]$ chromophore in the visible region, the rotational strength $R(A_2)$ is enhanced by polar and $R(E)$ by equatorial ligand groups. The correlation is employed to assign structures to anion-associations with $[Co(R\text{-}MeTACN)_2]^{3+}$.

The well-investigated D_3 tris(diamine)cobalt(III) complexes, which necessarily have the alkyl ligand groups located close to the equatorial XY plane of the complex, generally owe their chirality to, firstly, the skew mutual relationships of the mean planes of pairs of chelate rings, the configurational effect, and, secondly, to a puckered δ or λ conformation of each chelate ring, the conformational effect. The ligand, R-(-)-2-methyl-1,4,7-triazacyclononane, R-MeTACN, and the complex $[Co(R\text{-}MeTACN)_2]^{3+}$ (1), were synthesised[1] with the expectation, from molecular models, that the individual chelate rings of each ligand in the complex ion (1) have a common preferred λ-conformation, giving only conformational optical-activity due to alkyl ligand groups with a more polar location, closer to the $C_3(Z)$ axis.

The stereochemical expectation is confirmed by the X-ray crystal and molecular structure determination[2] of $[Co(R\text{-}MeTACN)_2]I_3.5H_2O$, which is optically-uniaxial, belonging to the space group R32, with the C_3 axis of each complex ion (1) parallel to the crystal c-axis. The CD spectrum of a single crystal of $[Co(R\text{-}MeTACN)_2]I_3.5H_2O$ with radiation propagated along the crystal c-axis measures the rotational strength R(E) of transitions polarized in the equatorial XY plane of the complex ion (1), whereas the corresponding solution CD spectrum additionally measures $R(A_2)$, giving the sum, $R(T_1) = R(A_2) + R(E)$. A comparison of the single-crystal and the aqueous solution CD spectra of $[Co(R\text{-}MeTACN)_2]^{3+}$ shows (Figure) that, of the two D_3 components of the d-d transition to the octahedral $^1T_1$ state of cobalt(III) near 21,000 cm^{-1}, the $^1A_1 \rightarrow {}^1E$ component has a negative and the minor rotational strength (R(E) = -0.16 Debye-Bohr magneton), while the component polarized along the C_3(Z) axis, $^1A_1 \rightarrow {}^1A_2$, has a positive and the major strength ($R(A_2) = +0.32\ D\beta_M$) as is shown by the sum ($R(T_1) = +0.16\ D\beta_M$) given by the solution CD spectrum.

In contrast, single-crystal and solution CD studies of the tris(1,2-diamine)cobalt(III) complexes show[3,4] that R(E) is generally the dominant rotational strength, governing the sign of the overall sum, $R(T_1)$. However, the polar capping of Λ-(+)-$[Co(en)_3]^{3+}$, either by hydrogen-bonding in the ion-association complex with the phosphate anion,[5] or covalently, by means of the hexadentate ligand,[6] 1,1,1-tris(2'-aminoethylaminomethyl)ethane, enhances $R(A_2)$ at the expense of R(E). The double polar-capping of Λ-(+)-$[Co(en)_3]^{3+}$, by treatment[7] with formaldehyde and ammonia to form (-)-[Co(1,3,6,8,10,13,16,19-octa-azabicyclo[6,6,6]-eicosane)]$^{3+}$, changes the overall rotational strength $R(T_1)$ from +0.047 to -0.068 $D\beta_M$, illustrating the general enhancement of $R(A_2)$ at the expense of R(E) by the addition of atoms or groups, whether covalent, ionic, or hydrogen-bonded, to the D_3 polar regions of the $[Co^{(III)}N_6]$ cluster.

In the crystal of $[Co(R\text{-}MeTACN)_2]I_3.5H_2O$ iodide ions are located on the C_3 axis of the complex ion (1) above the upper and below the lower of the two ligands.[2] A similar mutual steric relation between the anion and the complex cation may persist in solution. On the addition of 10^{-2}M iodide, the $\Delta\varepsilon$ maximum at 475 nm of the complex ion (1) in solution increases from +4.62 to +4.95, compared with the corresponding $\Delta\varepsilon$ value of +6.07 for the microcrystalline iodide salt of (1) dispersed in a solid matrix of CsCl (Figure). Thus the component rotational strength $R(A_2)$ of $[Co(R\text{-}MeTACN)_2]^{3+}$ is enhanced at the expense of R(E) on ion-association with iodide, an observation suggesting a polar location of the perturbing halide close to the C_3 axis of the complex ion (1) in solution.


λ/10² nm
5
4
3
2
100
ε
10
1
I⁻(10⁻²M)
I⁻..(10⁻⁴M)
ClO₄⁻
SeO₃²⁻
10⁻²M
0·1M
Δε/4
ν/10⁴ cm⁻¹
+2
0
Δε
Crystal axial Δε
-2
-4
-6
6
4
2
0
Δε
-2
-4
-6
Y
X
CH₃
CH₂
NH
C
H
CH₂
CH₂
Co
HN
NH
CH₂
CH₂

(1)

In contrast to the effect of the iodide ion, the multiply-charged oxyanions, phosphate, selenite, and dicarboxylate ions, reduce the area of the 475 nm CD band of $[Co(R\text{-}MeTACN)_2]^{3+}$ (Figure). In these cases R(E) is enhanced at the expense of $R(A_2)$, suggesting that oxyanions are located in the equatorial XY plane of the complex ion (1) in the ion-association formed in solution. Molecular models indicate the steric feasibility of bidentate hydrogen-bonding between a poly-oxyanion in the D_3 equatorial plane and a N-H group of the upper and of the lower ligand in the complex ion (1), but rule out a polar capping of the complex by H-bonding along the $C_3(Z)$ axis, analogous to the Λ-(+)-$[Co(en)_3][PO_4]$ case.[5]

An alternative but less-probable origin of the observed CD changes (Figure) is a conformational change in the ligands of the complex ion (1) on association with an oxyanion in solution. The CD spectrum of $[Co(R\text{-}MeTACN)_2](ClO_4)_3$ in methanol solution is invariant with respect to temperature over the range 120 to 300 K and is virtually identical to that of the corresponding aqueous solution at ambient temperature (Figure), suggesting that the ligands have no significant conformational lability in $[Co(R\text{-}MeTACN)_2]^{3+}$.

First-order ligand-polarization calculations[4] of the rotational strengths of $[Co(R\text{-}MeTACN)_2]^{3+}$, based upon the atomic coordinates of the complex (1) determined in the X-ray study,[2] give the values, +0.66, -0.64, +0.02 $D\beta_M$ for $R(A_2)$, R(E) and $R(T_1)$, respectively. While the calculated values have the correct sign, they are not satisfactory quantitatively.

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References

(1) S. F. Mason and R. D. Peacock, Inorg. Chim. Acta, 19, 75 (1976).

(2) M. Mikami, R. Kuroda, M. Konno and Y. Saito, Acta Cryst., B33, 1485 (1977).

(3) R. Kuroda and Y. Saito, Bull. Chem. Soc. Japan, 49, 433 (1976).

(4) S. F. Mason and R. H. Seal, Molec. Phys., 31, 755 (1976).

(5) S. F. Mason and B. J. Norman, J. Chem. Soc.(A), 307 (1966); E. N. Duesler and K. N. Raymond, Inorg. Chem., 10, 1486 (1971).

(6) J. E. Sarneski and F. L. Urbach, J. Amer. Chem. Soc., 93, 884 (1971).

(7) I. I. Creaser, J. M. Harrowfield, A. J. Herlt, A. M. Sargeson, J. Springborg, R. J. Gene, and M. R. Snow, J. Amer. Chem. Soc., 99, 3181 (1977).

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