Metal dithiolenes[21] are well-known and very stable species in condensed phases. With this type of compound, all the nonpolysulfide masses in the $V^+$, ethylene sulfide system can be rationalized. (see Table I). The "dithiolenes" appear at high pressure relative to the polysulfide species and appear to be far less reactive.

The "dithiolene" type structures are indicated only because of their solution analogues and their apparent fit to the observed masses. Additional sulfurs may occupy vacant coordination sites or even insert into the ring system as has been seen in solution for dithiolate complexes,[22] but there is no experimental basis for any of these structures. Indeed, we make no claims as to the structure of the metal polysulfides although we assume that rings are involved on the basis of the work cited earlier and the fact that at least eight attachments have been seen. ICR photodissociation[23,24] techniques allow indirect observation of the optical absorption spectra of gas-phase ions, which should allow better estimates of the structures to be made. We are curently modifying our instrument to allow simultaneous laser ionization, photodissociation experiments.

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**Registry No.** Ethylene sulfide, 420-12-2; Fe, 7439-89-6; Co, 7440-48-4; V, 7440-62-2; Ti, 7440-32-6; Al, 7429-90-5.

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Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

**T. J. Carlin**
**M. B. Wise**
**B. S. Freiser***

*Received October 23, 1980*

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## Absolute Configuration and Circular Dichroism of the Lanthanide Complex Trisodium Tris(oxydiacetato)europate(III) Bis(sodium tetrafluoroborate) Hexahydrate

*Sir:*

We report the first correlation of circular dichroism (CD) and absolute configuration in a lanthanide complex. Single crystals of the title compound, $Na_3Eu(C_4H_4O_5)_3{\cdot}2NaBF_4{\cdot}6H_2O$, were prepared as follows. A stoichiometric amount of $Eu_2O_3$ was dissolved in $C_4H_4O_5H_2$ (oxydiacetic acid). This is a fairly strong acid, and the $Eu_2O_3$ dissolves easily at room temperature. The resultant solution was brought to neutral pH by addition of NaOH solution. A 2 molar ratio of $NaBF_4$ was added to this solution. Crystals were grown by slow evaporation at ambient temperature in Teflon beakers. This procedure is similar to that used previously to prepare the $ClO_4^-$ double salts[1-3] $Na_3Ln(C_4H_4O_5)_3{\cdot}2NaClO_4{\cdot}6H_2O$. The morphologies of the tetrafluoroborate and perchlorate salts are identical.

Table I. Spectroscopic Parameters for $Na_3Eu(C_4H_4O_5)_3{\cdot}2NaBF_4{\cdot}6H_2O$ at Room Temperature

| transition | energy | rotational strength[a] | dipole strength[b] | $g$[c] |
|---|---|---|---|---|
| $^7F_0(A_1) \rightarrow {}^5D_1(E)$ | 18 981 | $-0.13 \times 10^{-42}$<br>$(-400)$[e] | $1.3 \times 10^{-42}$<br>$(0.7)$[e] | −0.42 |
| $^7F_0(A_1) \rightarrow {}^5D_2(2E)$[d] | 21 490 | $-0.10 \times 10^{-42}$<br>$(-200)$ | $3.2 \times 10^{-42}$<br>$(1.4)$ | −0.13 |

[a] In units of $esu^2\ cm^2$. The numbers in parentheses are the peak $[\theta]$ values (deg dL $dm^{-1}\ mol^{-1}$). All values have an error of ±20%. [b] In units of $esu^2\ cm^2$. The numbers in parentheses are the peak $\epsilon$ values ($cm^2\ mol^{-1}$). [c] $g = 4R/D$. [d] This is the higher energy $E$ level. [e] The two bands have different bandwidths so the ratios of $\epsilon$'s and $[\theta]$'s are not directly proportional to the ratios of dipole strengths and rotational strengths.

Table II. Coordinates of $Na_3Eu(C_4H_4O_5)_3{\cdot}2NaBF_4{\cdot}6H_2O$ with Respect to Rhombohedral Axes

| atom[a] | $x$ | $y$ | $z$ |
|---|---|---|---|
| Eu | 0 | 0 | 0 |
| Na(1) | 0.2145 (4) | 0.7855 | 0.5 |
| Na(2) | 0.8007 (1) | 0.8007 | 0.8007 |
| B | 0.5707 (4) | 0.5707 | 0.5707 |
| F(1) | 0.4684 (2) | 0.4835 (2) | 0.7068 (2) |
| F(2) | 0.6187 (3) | 0.6187 | 0.6187 |
| O(1) | 0.2573 (4) | −0.2573 | 0 |
| O(2) | −0.0294 (1) | −0.2509 (1) | 0.1041 (1) |
| O(3) | 0.0624 (2) | −0.5161 (1) | 0.1541 (2) |
| O(W) | 0.0781 (2) | 0.7115 (2) | 0.7824 (1) |
| C(1) | 0.2564 (2) | −0.4148 (2) | 0.0624 (2) |
| C(2) | 0.0828 (1) | −0.3941 (1) | 0.1134 (1) |
| H(1) | 0.281 (3) | −0.480 (4) | 0.165 (4) |
| H(2) | 0.334 (3) | −0.466 (3) | −0.008 (3) |
| H(W1) | 0.091 (4) | 0.827 (4) | 0.744 (4) |

[a] The numbering system is shown in Figure 1 and is consistent with ref 1–3.

Table III. Bond Distances (Å) in $Na_3Eu(C_4H_4O_5)_3{\cdot}2NaBF_4{\cdot}6H_2O$

| | | | |
|---|---|---|---|
| Na(1)–O(3) | 2.583 (3) | Eu–O(1) | 2.495 (2) |
| Na(1)–F(1) | 2.337 (5) | Eu–O(2) | 2.395 (2) |
| Na(1)–O(W) | 2.292 (4) | O(1)–C(1) | 1.418 (3) |
| Na(2)–O(3) | 2.347 (4) | C(1)–C(2) | 1.518 (4) |
| Na(2)–O(W) | 2.474 (5) | C(2)–O(2) | 1.263 (2) |
| B–F(1) | 1.382 (4) | C(2)–O(3) | 1.240 (2) |
| B–F(2) | 1.365 (4) | | |

Table IV. Selected Bond Angles (Deg) in $Na_3Eu(C_4H_4O_5)_3{\cdot}2NaBF_4{\cdot}6H_2O$

| | | | |
|---|---|---|---|
| O(1)–Eu–O(2) | 63.4 (1) | O(3)–Na(1)–O(3) | 101.4 (2) |
| O(1)–Eu–O(2) | 74.3 (1) | O(3)–Na(1)–F(1) | 85.1 (2) |
| O(1)–Eu–O(2) | 135.9 (1) | O(3)–Na(1)–F(1) | 172.6 (2) |
| O(2)–Eu–O(2) | 77.9 (1) | O(3)–Na(1)–O(6) | 82.8 (2) |
| O(2)–Eu–O(2) | 88.1 (1) | O(3)–Na(1)–O(6) | 87.6 (2) |
| O(2)–Eu–O(2) | 126.7 (1) | F(1)–Na(1)–F(1) | 88.6 (3) |
| O(2)–Eu–O(2) | 148.6 (1) | F(1)–Na(1)–O(6) | 89.7 (2) |
| C(1)–O(1)–C(1) | 115.2 (2) | F(1)–Na(1)–O(6) | 101.2 (2) |
| O(1)–C(1)–C(2) | 109.1 (2) | O(6)–Na(1)–O(6) | 164.8 (2) |
| C(1)–C(2)–O(2) | 117.7 (3) | O(3)–Na(2)–O(3) | 104.9 (2) |
| C(1)–C(2)–O(3) | 118.1 (2) | O(3)–Na(2)–O(6) | 84.1 (2) |
| O(2)–C(2)–O(3) | 124.7 (3) | O(3)–Na(2)–O(6) | 85.9 (2) |
| F(1)–B–F(1) | 108.7 (3) | O(3)–Na(2)–O(6) | 163.5 (2) |
| F(1)–B–F(2) | 110.1 (3) | O(6)–Na(2)–O(6) | 82.6 (2) |

X-ray and CD/absorption data were recorded from fragments of the same large crystal. The CD/absorption data were collected at ambient temperature with use of Jasco J-20 spectropolarimeter, which has had an absorption mode added to it, interfaced with a Spex 0.85-m double monochromator. All spectra are sample limited in resolution. Table I gives some of the CD/absorption data. Within experimental error, these data are identical with those for the $ClO_4^-$ salt,[4-5] where all other observed transitions, $^7F_1 \rightarrow {}^5D_{0-2}$, also have a negative

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**Table V.** Thermal Parameters[a]

| atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Eu | 0.00622 (1) | 0.00622 | 0.00622 | −0.00528 (1) | −0.00528 | −0.00528 |
| Na(1) | 0.01677 (16) | 0.01677 | 0.0128 (1) | −0.0159 (2) | −0.0090 (2) | −0.0090 |
| Na(2) | 0.00999 (8) | 0.00999 | 0.00999 | −0.0078 (1) | −0.0078 | −0.0078 |
| B | 0.0135 (3) | 0.0135 | 0.0135 | −0.0109 (3) | −0.0109 | −0.0109 |
| F(1) | 0.0187 (2) | 0.0271 (2) | 0.0180 (2) | −0.0280 (2) | −0.0023 (3) | −0.0157 (3) |
| F(2) | 0.0308 (2) | 0.0308 | 0.0308 | −0.0282 (2) | −0.0282 | −0.0282 |
| O(1) | 0.00756 (13) | 0.00756 | 0.0120 (1) | −0.0049 (2) | −0.0080 (2) | −0.0080 |
| O(2) | 0.00946 (8) | 0.00763 (8) | 0.0122 (1) | −0.0075 (1) | −0.0084 (1) | −0.0075 (1) |
| O(3) | 0.01428 (11) | 0.00867 (8) | 0.0189 (1) | −0.0108 (1) | −0.0120 (2) | −0.0103 (1) |
| O(W) | 0.01937 (12) | 0.01280 (10) | 0.0134 (1) | −0.0127 (1) | −0.0166 (1) | −0.0094 (1) |
| C(1) | 0.01008 (12) | 0.00744 (11) | 0.01407 (14) | −0.0053 (1) | −0.0116 (2) | −0.0078 (2) |
| C(2) | 0.00998 (9) | 0.00728 (7) | 0.00880 (9) | −0.0082 (1) | −0.0070 (1) | −0.0056 (1) |

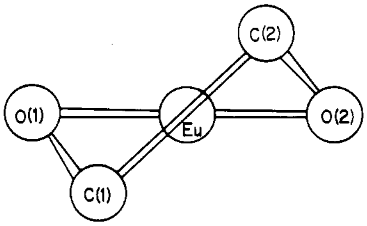
| atom | $B$, Å$^2$ | atom | $B$, Å$^2$ | atom | $B$, Å$^2$ |
|---|---|---|---|---|---|
| H(1) | 4.9 (9) | H(2) | 3.2 (6) | H(W1) | 9.2 (17) |

[a] The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

CD. Absorption and CD spectra have also been recorded for the $Pr^{3+}$ oxydiacetate[6] with $ClO_4^-$ and $BF_4^-$ counterions; at room temperature the spectra are identical for these two salts.

X-ray data were collected with the use of Mo K$\alpha$ radiation at ambient temperature with an Enraf-Nonius CAD-4 automatic diffractometer. A total of 1926 unique reflections with $1° \leq \theta \leq 33°$ was measured. All but one had $I > 3\sigma(I)$ and were used in the refinement. Like the $ClO_4^-$ salts,[1-3] the crystals are rhombohedral, of space group $R32$, with $Z = 1$, and have unit cell dimensions $a = 10.898$ (1) Å and $\alpha = 52.83$ (1)°. Coordinates from ref 1 were used as a starting point, and the structure was refined to an $R = 0.032$. However, 14 reflections had $||F_o| - |F_c||$ between $8\sigma(F_o)$ and $22\sigma(F_o)$. Refinement of the alternate enantiomorph yielded $R = 0.019$ and no discrepancies greater than $5\sigma(F_o)$. The atomic coordinates, bond distances, and bond angles for this enantiomorph are given in Tables II–IV.

The tris(oxydiacetato)europate(III) ion is shown in Figure 1. The absolute configuration was found to be $\Delta([\lambda,\lambda], [\lambda,\lambda], [\lambda,\lambda])$. Here each square bracket refers to one oxydiacetate ligand and each $\lambda$ refers to one of the two five-membered rings per ligand as shown.[7]



The actual deviation from planarity in the ring is quite small; C(1) is −0.037 (2) Å and C(2) is +0.023 (1) Å from the O(1)–Eu–O(2) plane, and the torsion angle O(1)–C(1)–C(2)–O(2) is only 4.70°.

There are no remarkable differences in the gross structural features of the $ClO_4^-$ and $BF_4^-$ compounds, although the precision of the present determination is much higher. This higher precision is important when the CD is considered. Recently it has been shown that very small differences in bond lengths can bring about dramatic changes in the calculated CD.[4,5] Changes in bond lengths as small as 0.01 Å (close to the limiting error given for the structures of the $ClO_4^-$ compounds[2,3]) can invert the relative signs of the CD of the ${}^7F_0 \rightarrow {}^5D_1$ and ${}^7F_0 \rightarrow {}^5D_2$ transitions calculated for the $Eu(C_4H_4O_5)_3^{3-}$ species. Calculations which used values for the Eu–O(1) and Eu–O(2) bond distances extrapolated from previous data gave the incorrect result, while it appears that use of the present data will lead to relative signs that agree with experiment.[4] This apparent sensitivity to stereochemistry means that CD may be of marginal value in predicting absolute configurations for lanthanide complexes.

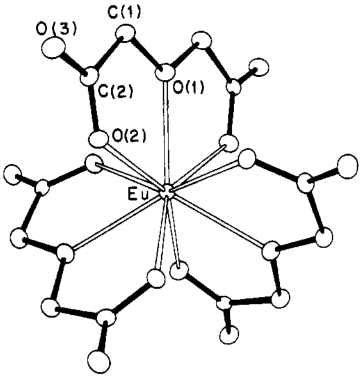


**Figure 1.** Tris(oxydiacetato)europate(III) ion viewed down the threefold crystal and molecular axis.

Another structural parameter of importance in determining the molecular chirality is the twist angle between the triangles of carboxylic oxygen atoms above and below the metal. In the present case, the front triangle is twisted 16.3° clockwise with respect to the back triangle.

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**Registry No.** $Na_3Eu(C_4H_4O_5)_3 \cdot 2NaBF_4 \cdot 6H_2O$, 77254-97-8.

Department of Chemistry
Louisiana State University
Baton Rouge, Louisiana 70803

**Frank R. Fronczek**
**Asok K. Banerjee**
**Steven F. Watkins**
**Robert W. Schwartz***

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(7) This is the standard definition; see, for example, "Advanced Inorganic Chemistry", F. A. Cotton and G. Wilkinson, 4th ed., Wiley, New York, 1980, p 79.

*To whom correspondence should be addressed at the Chemistry Division, Naval Weapons Center, China Lake, CA 93555.