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Left column

3r]Br$_2$.[7] Samples were prepared
mg of sample per 400 mg of KBr
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LEXES IN cm^{-1}

Sym. Def.	Rocking
1320 (w.Sh.)	778 (s.S.)
1293 (s.S.)	
1258 (m.Sh.)	
1290 (s.S.)	763 (s.S.)
1260 (w.S.)	
1285 (s.S.)	760 (s.S.)
1254 (w.S.)	
1297 (s.S.)	840 (m.S.)
1275 (m.S.)	768 (s.S.)
	732 (s.S.)
1290 (s.S.)	840 (m.S.)
	765 (s.S.)
	730 (s.S.)
1370 (s.D.)†	914 (w.Sh.)†
1290 (s.S.)	890 (w.S.)†
1240 (s.S.)†	822 (w.S.)‡
	800 (s.S.)†
	730 (m.Sh.)‡
1390 (s.D.)†	914 (w.Sh.)†
1290 (s.S.)	890 (w.S.)†
1250 (m.S.)†	800 (s.S.)†
	765 (s.S.)
1286 (s.S.)	775 (s.S.)
1252 (m.S.)	725 (m.Sh.)
1348 (m.S.)	805 (m.S.)
1318 (s.S.)	758 (m.S.)
1380 (s.S.)†	885 (m.S.)†
1305 (m.S.)	805 (s.S.)†
1252 (s.S.)†	740 (s.S.)
1395 (s.S.)†	890 (m.S.)†
1300 (m.S.)	808 (s.S.)†
1280 (s.S.)	735 (m.D.)
1262 (m.Sh.)†	
1401 (w.S.)	725 (s.S.)
1281 (s.S.)	
1400 (m.S.)	730 (m.S.)
1282 (s.S.)	
1269 (Sh.)	

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Springer, Berlin (1951).

Right column

slight concentration dependence on the position of this band, however, concentration is held approximately constant to permit comparison of relative positions. A Beckman IR-5 was used to decide optimum concentrations and all data reported here were obtained with a Perkin-Elmer Model 21 Spectrophotometer equipped with sodium chloride optics.

DISCUSSION

It has previously been observed that both the rocking and symmetrical deformation frequencies increase, in general, with increasing positive charge on the complex unit of platinum, palladium(II) and cobalt(III) ammine compounds.[4] The data for chromium(III) complexes are shown in Table 1. The reported values[3] of the symmetrical deformation and rocking frequencies for $[Cr(NH_3)_6]Br_3$ are 1318 and 797 cm^{-1} respectively. Comparing these values with those of Table 1 for Cr(III) pentammine, tetrammine and triammine bromides shows that this trend is approximately true for the rocking frequencies only. Furthermore, the frequency shifts observed in the stretching, symmetric and rocking deformation regions from variation of the anion outside the coordination sphere are in accord with theories of hydrogen bonding in all cases except that of the aquo complexes. No systematic trend was found in the stretching frequency when the anion inside the coordination sphere was varied. Geometrical isomerism has also been shown to produce some systematic infrared spectral variations in ammine complexes.[10] However, chemical evidence indicates that the two green halotetrammines studied here have the same isomeric configurations.[7] Observed shifts in the rocking and deformation regions occur in the reverse direction when these frequencies of the two halotriammines are compared, although these shifts are small. This reversal of expected trends could be due to incorrect structural assignments of these two complexes. Although no structural studies have been reported, the aquation product of $[Cr(NH_3)_3Cl_3]$ suggests that it is $[Cr(NH_3)_4Cl_2]$ $[Cr(NH_3)_2Cl_4]$ instead of the neutral complex.[11]

When a single univalent anion inside the coordination sphere is varied, shifts in the rocking and deformation regions are in the same direction as those expected for the uncoordinated anion. If the triammines are excluded, shifts in the rocking and deformation regions become progressively smaller as one varies the number of univalent anions inside the coordination sphere.

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[10] J. P. Faust and J. V. Quagliano, *J. Amer. Chem. Soc.* **76**, 5346 (1954).
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Europium thenoyltrifluoroacetonate, preparation and fluorescence properties

During the last several years there has been a resurgence of interest in the fluorescence properties of rare-earth chelates, due to the possible use of such compounds in laser (optical maser) devices.[1-3] One compound that has been investigated by several workers[3-6] is europium thenoyltrifluoroacetonate, [Eu(TTA)$_3$; I, R_1 = 2-thienyl, F_2 = trifluoromethyl].* In these previous studies, however,

* The systematic name for this compound is tris-(4,4,4,-trifluoro-1-(2-thienyl)-1,3-butanediono)-europium(III).

[1] A. Lempicki and H. Samelson, *Phys. Letters* **4**, 133 (1963).
[2] A. Lempicki and H. Samelson, *Appl. Phys. Letters* **2**, 159 (1963).
[3] N. E. Wolff and R. J. Pressley, *Appl. Phys. Letters* **2**, 152 (1963).
[4] C. W. Kuhlman, Jr., Ph.D. Thesis, Washington University (1953).
[5] H. Winston, O. J. Marsh, C. K. Suzuki and C. L. Telk, *J. Chem. Phys.* **39**, 267 (1963).
[6] R. A. Gudmundsen, O. J. Marsh and E. Matovich, *J. Chem. Phys.* **39**, 272, (1963).

the compositions of the materials employed have been either unreported or ill-defined. In particular, MARSH and co-workers[5,6] found that their material contained nitrogen (from the piperidine used in the preparation) and the elemental analyses corresponded to no simple empirical formula. The presence of foreign molecules (particularly if bonded as part of a mixed ligand complex) can result in very large changes in the luminescence properties of europium chelates.[7-9]
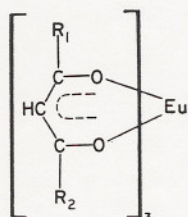
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We report here a simple procedure by which the dihydrate of $Eu(TTA)_3$ can be obtained in good yield and purity. We also report some of the properties of this compound and compare them with those of other europium β-diketone chelates of known composition and purity.

EXPERIMENTAL

Europium thenoyltrifluoroacetonate

Thenoyltrifluoroacetone* (6·67 g, 0·03 moles) was dissolved in 75 ml 95% ethanol and 30 ml (0·03 moles) 1 M aqueous ammonia added. To the resulting clear solution was added 0·01 mole $EuCl_3$ (Lindsay 99·9 per cent added as the calculated volume of standardized 0·5 M solution) in 120 ml water. The mixture was allowed to stand several hours until the initially formed oil solidified. The yellow solid (6·8 g) was filtered off, washed with water and dried in a vacuum desiccator. The compound was recrystallized by dissolving in 15 ml acetone, filtering and reprecipitating with 100 ml water. The product separated as an oil which solidified on standing. It was dried *in vacuo* at room temperature. Elemental analyses showed the recrystallized product to contain excess thenoyltrifluoroacetone. This was removed by stirring the solid with 25 ml petroleum ether for $\frac{1}{2}$ hr. The excess chelating agent was extracted into the liquid while the chelate remained undissolved. Yield of vacuum-dried solid 5·9 g. Anal. Calcd. for $(C_8H_4O_2F_3S)_3Eu\cdot2H_2O$: C, 33·9; H, 1·89; Eu, 17·8. Found: C, 33·8; H, 1·83; Eu, 18·0%. Principal infrared absorption peaks (Nujol mull): 3·05, 6·28, 6·53, 6·67, 7·16, 7·43, 7·76, 8·03, 8·20, 8·36, 8·48, 8·82, 8·88, 9·33, 9·49, 9·68, 9·73, 9·96, 10·79, 10·86, 11·68, 12·67, 12·79, 13·12, 13·40, 13·72, 14·14, 14·52, 14·78 μ. Appreciable differences were noted between this spectrum and the corresponding one obtained with the KBr pellet technique, possibly due to interaction between the KBr and chelate during the pressing procedure.

Europium dibenzoylmethide $(Eu(DBM)_3$; I, $R_1 = R_2 =$ phenyl)

The monohydrate was prepared by the procedure previously described.[10]

Europium benzoylacetonate $(Eu(BA)_3$; I, $R_1 =$ phenyl, $R_2 =$ methyl)

The dihydrate was obtained by the same procedure as that used for the dibenzoylmethide.[10] Anal. Calcd. for $(C_{10}H_9O_2)_3Eu\cdot2H_2O$: C, 53·7; H, 4·65; Eu, 22·6. Found: C, 53·8; H, 4·67; Eu, 22·7%.

* It is important to use anhydrous thenoyltrifluoroacetone rather than the monohydrate. The hydrate hydrolyses much more rapidly than the anhydrous form, even when both are in the presence of excess water. P. CROTHER and F. L. MOORE, *Analyt. Chem.* **35**, 2081 (1963).

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[10] R. G. CHARLES and A. PERROTTO, *J. Inorg. Nucl. Chem.* **26**, 373 (1964).

Europium acetylaceto

The procedure of for $(C_5H_7O_2)_3$ Eu·2H

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Fluorescence characteristics

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[15] E. V. SAYRE and S. FREED,

Europium acetylacetonate (Eu(AA)$_3$; I, R$_1$ = R$_2$ = methyl)

The procedure of STITES[11] gave the dihydrate when air-dried at room temperature. Anal. Calcd. for (C$_5$H$_7$O$_2$)$_3$ Eu·2H$_2$O: C, 37·1; H, 5·19; Eu, 31·3%. Found: C, 37·6; H, 5·08; Eu, 31·4%.

Ultraviolet absorption spectra

Spectra of the hydrated compounds were obtained with a Cary model 14 spectrophotometer and 2 mm or 1 cm matched quartz cells. Concentrations, in absolute ethanol, were in the range 2×10^{-5} to 1×10^{-4} M.

Thermogravimetric analysis

The thermobalance has been previously described.[12] Fifty milligram samples were heated in shallow platinum crucibles in an atmosphere of flowing argon (50 ml/min). The heating rate was 2°C/min. The weight-temperature curves were recorded automatically with a Mosely X-Y recorder.

Fluorescence measurements

The fluorescence spectrum at 25°C was determined at 1 Å resolution with a 1-m Jarrell-Ash spectrometer, as previously described.[13] The spectrum has nor been corrected for the decrease in sensitivity above 630 mμ.[13]
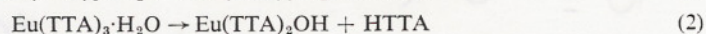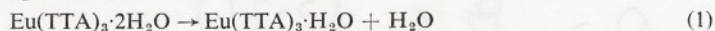
Fluorescence decay times were calculated from oscilloscope traces of fluorescence vs. time. Fluorescence was excited with the light from a Xenon flash tube.

Relative fluorescence intensities were determined with an EM19558 photomultiplier, utilizing a 610 mμ interference filter to isolate the fluorescence from the $^5D_0$–$^7F_2$ transitions.

RESULTS AND DISCUSSION

Thermogravimetric analysis

Figure 1 shows the weight loss-temperature curve obtained by heating Eu(TTA)$_3$·2H$_2$O in an inert atmosphere. Weight loss to 110°C (2·4%) corresponds to the loss of one water molecule (calculated weight loss for Equation (1), 2·12%).

$$Eu(TTA)_3 \cdot 2H_2O \rightarrow Eu(TTA)_3 \cdot H_2O + H_2O \qquad (1)$$

$$Eu(TTA)_3 \cdot H_2O \rightarrow Eu(TTA)_2OH + HTTA \qquad (2)$$

Further heating to higher temperatures, however, does not give a weight plateau corresponding to anhydrous Eu(TTA)$_3$. The latter species, if formed, is apparently not stable at the temperatures required for complete dehydration. An alternate explanation for the observed weight-loss curve in Fig. 2 involves the hydrolysis reaction 2, in which case the second water molecule is not evolved as such. In any event, Fig. 2 shows that anhydrous Eu(TTA)$_3$ is not readily obtained by thermal dehydration of the dihydrate at atmospheric pressure. In a number of attempts, we have been equally unsuccessful in obtaining the anhydrous form by heating the hydrate *in vacuo*.

Ultraviolet absorption spectra

In Fig. 2 the ultraviolet absorption spectrum of Eu(TTA)$_3$·2H$_2$O is compared with the spectra of other europium β-diketone chelates. The spectrum resembles those of the phenyl-substituted chelates Eu(DBM)$_3$ and Eu(BA)$_3$. The long wavelength band of the chelates increases in both wavelength and intensity in the order Eu(AA)$_3$ < Eu(BA)$_3$ < Eu(TTA)$_3$ < Eu(DBM)$_3$. This order probably represents increasing participation of reasonance structures involving phenyl or thienyl groups with the chelate rings. A similar progression toward longer wavelength and more intense absorption with increasing number of phenyl groups occurs with the longer wavelength band of the *p*-polyphenyl series of compounds.[14]

Fluorescence characteristics

Figure 3 shows the fluorescence spectrum at 25°C of solid Eu(TTA)$_3$·2H$_2$O. The spectrum is typical of that obtained from Eu^{3+} in crystals,[15] and is due to transitions within the $4f^6$ electron

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[12] R. G. CHARLES and A. LANGER, *J. Phys. Chem.* **63**, 603 (1959).
[13] R. G. CHARLES and R. C. OHLMANN, *J. Inorg. Nucl. Chem.* In press.
[14] A. E. GILLAM and D. H. HEY, *J. Chem. Soc.* 1170 (1939).
[15] E. V. SAYRE and S. FREED, *J. Chem. Phys.* **24**, 1211, 1213 (1956).

17

Notes

FIG. 1.—Thermogravimetric curve for europium thenoyltrifluoroacetonate dihydrate heated in a stream of argon.

FIG. 2.—Ultraviolet absorption spectra of europium(III) β-diketone chelates in ethanol.

FIG. 3.—Fluorescence spectrum of solid europium thenoyltrifluoroacetone dihydrate at 25°C.

shell. The various groups of lines arise from transitions from the $^5D_0$ metastable state to various terminal levels as follows: $^7F_0$ (579 mμ), $^7F_1$(585–600 mμ), $^7F_2$ (611·5, 615·4, and 620·5 mμ), $^7F_3$ (648–660 mμ), $^7F_4$ (688–706 mμ). The terminal states, excluding $^7F_0$, are split 200–500 cm^{-1} by the ligand interactions.

There is a considerable difference in the structure of the strong groups of lines due to the $^5D_0 \rightarrow ^7F_2$ transition from that reported by WINSTON et al.[5] Since they presumably were measuring a piperidine adduct rather than the hydrate of Eu(TTA)$_3$, this difference might be expected in view of the results we have reported on the fluorescence spectra of Eu(DBM)$_3$ adducts.[13] In earlier work,[9]

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[1] S. M. JORGENSEN, Z.
[2] J. LECOMTE and C. D
[3] R. B. PENLAND, T. J
[4] J. R. BEATTIE and D
[5] R. K. MURMANN and
[6] V. B. ADELL, Z. anoi
[7] S. E. BEACOM, Ph.D
[8] F. BASOLO and G. S.

we showed that there was considerable variation in the character of the ligand field splitting, as well as in the intensity and decay times of the fluorescence, when complexes were formed between $Eu(DBM)_3$ and Lewis bases. A comparison of the fluorescence spectrum of $Eu(TTA)_3 \cdot 2H_2O$ with those of $Eu(DBM)_3$ and its adducts[13] shows that the greatest similarity occurs with anhydrous $Eu(DBM)_3$ rather than with $Eu(DBM)_3 \cdot H_2O$ or any of the other adducts studied. Such a similarity indicates that similar ligand fields prevail about the Eu^{3+} in the two compounds.

The measured fluorescence decay time of solid $Eu(TTA)_3 \cdot 2H_2O$ was 265 μsec at room temperature and 310 μsec at 77°K. The fluorescence intensity at room temperature was 65% of that at 77°K. As a result of smaller temperature quenching the fluorescence intensity of $Eu(TTA)_3 \cdot 2H_2O$ at room temperature is approximately 45 times as great as that of $Eu(DBM)_3 \cdot H_2O$ at the same temperature[9] (intensities integrated over the 610–620 mμ region). The fluorescence intensities of the two compounds are comparable at 77°K.

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Pittsburgh 35, Pa.   R. C. OHLMANN

The nitro → nitrito transition in nitropentamminecobalt(III) complexes

THE linkage isomerism of the NO_2^- group in cobalt(III) ammine complexes was first noted by JORGENSEN.[1] Although many studies have been reported on this subject,[2–5] all of them have been concerned with the nitrito → nitro transition either in solution or in the solid state. It is well known that the above transition takes place, say in the $[Co(NH_3)_5ONO]X_2$ complexes, on standing at room temperature for several days, or more rapidly by heating.

ADELL[6] found that the reverse transition could be initiated by allowing $[Co(NH_3)_5NO_2]Cl_2$ to stand in sunlight for a long period of time. Similarly, BEACOM[7] found that ultraviolet radiation caused a color change in $[Co(NH_3)_5NO_2]Cl_2$, but the new product was not identified. In a more thorough investigation, BASOLO and HAMMAKER[8] found that ultraviolet radiation caused a nitro → nitrito transition in $[Ir(NH_3)_5NO_2]Cl_2$.

We wish to report here the ultraviolet radiation induced nitro → nitrito transition on the complexes, $[Co(NH_3)_5NO_2]X_2$, where X is Cl^-, Br^-, I^-, and NO_3^-. The reflectance spectra of a sample of $[Co(NH_3)_5NO_2]Br_2$, both before and after ultraviolet irradiation, are given in Fig. 1. As can be seen, the 460 mμ peak in the curve shifted to 485 mμ after an irradiation period of two one minute intervals. Further irradiation, up to four 1-min intervals, did not further charge the curve peak maximum. On heating the irradiated sample to 70° for 5 min, the curve peak shifted back to 460 mμ again, indicating the reformation of the nitrocomplex, $[Co(NH_3)_5NO_2]Br_2$.

Similar changes were noted for the other $[Co(NH_3)_5NO_2]X_2$ ($X = Cl^-$, I^-, and NO^{3-}) complexes. The peak maxima shifts, after irradiation of the nitro-complexes, were: chloride 455 → 475 mμ (ADELL[6] reported a 455 mμ peak for the NO_2^- and 480 mμ for the ONO-complexes); iodide, no definite curve peaks due to strong absorption below 500 mμ but a definite colour change of yellow to orange was evident; and nitrate, 460 → 480 mμ.

Exposure of the complexes, *cis*-$[Co(NH_3)_5(NO_2)_2]NO_3$, *cis*- and *trans*-$[Co(en)_2(NO_2)_2]NO_3$, and $[Co(NH_3)_3(NO_2)_3]$, to ultraviolet irradiation resulted in no change in their reflectance spectra. Thus, the nitro → nitrito transition appeared to be limited only to the mono-nitro complexes.

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[7] S. E. BEACOM, Ph.D Thesis, University of Connecticut (1954).
[8] F. BASOLO and G. S. HAMMAKER, Inorg. Chem. 1, 1 (1962).

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