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A Critical Examination of Some Methods for the Preparation of Tris and Tetrakis Diketonates of Europium(III)

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Several of the more versatile methods for the preparation of tris and tetrakis diketonate complexes of europium(III) are examined critically and modifications recommended where appropriate.

Introduction

For some time there has been considerable interest[1,2,3,4] in the light absorption and emission properties of certain diketonates of lanthanides, particularly europium(III) and terbium. Two classes of complexes may be distinguished depending on whether the ratio of diketonate ion to metal ion in the product is 1:3 (triscomplex) or 1:4 (tetrakiscomplex). Several methods expected to be of fairly general applicability in the preparation of one or other of these classes of chelate have been described.[4,5,6,7,8] However, the success or otherwise of a particular method would appear to depend on several factors and the desired product is not always readily obtained. In order to carry out a study of Mössbauer and other spectroscopic properties it became necessary for the present authors to prepare a range of such substances. Consequently, in the work described here some of the main methods for the preparation of tris and tetrakis complexes of europium(III) are examined critically in an attempt to improve the purity and yield of the required substances. Factors affecting the nature and yields of products are discussed.

In the account which follows the various diketones from which the ligands are derived, ostensibly by removal of a hydrogen ion, are represented by the abbreviations given in Table I.

Experimental Section

Chemicals. HDBM and HTTA (both 'Puriss' grade), HBTA and HTFA ('Pure' grade) were obtained from Koch-Light Ltd., Colnbrook, England. British Drug Houses, Poole, England supplied 'Laboratory Reagent' grade HAA, HBA, HHFA and piperidine. These substances were all used without further purification. Hydrated salts of europium(III) chloride and europium(III) nitrate were prepared by dissolution of europium(III) oxide (3N quality from Koch-Light) in hydrochloric and nitric acid respectively, concentrating the solution to near dryness on a hot-plate and finally drying over solid sodium hydroxide in a vacuum desiccator.

Preparative procedures recommended, following work on appropriate published methods of preparation of individual chelates, are set out below along with some relevant observations on the reactions involved.

Tris Diketonates

Eu(DBM)$_3$. The method of Whan and Crosby[6] was used to prepare first the piperidinium salt of the tetrakis chelate which on heating at 135°C under vacuum for 24 hours gave the anhydrous tris diketonate without difficulty.

Eu(BTA)$_3$. 2H$_2$O. The dihydrate was obtained by the method of Ismail *et al.*[9] It was purified by recrystallisation from toluene. Larger crystals of the substance may be obtained by addition of water to an acetone solution.

Eu(BA)$_3$. 2H$_2$O; Eu(TFA)$_3$. 2H$_2$O; Eu(HFA)$_3$. 2H$_2$O. The sodium salt (3 mmole) of the ligand in ethanol (25 ml) was added dropwise over a period of about 2 hours to a stirred aqueous solution (25 ml) of europium chloride (1 mmole). The sodium salts were prepared by mixing HTFA or HHFA with ethanolic sodium hydroxide (1:1 mole ratio) and treating HBA with sodium (1:1 mole ratio) under reflux in xylene.

With BA$^-$ as ligand, the chelate precipitated during the addition, but the mixture was set aside overnight before filtration. The precipitate was air dried; recrystallisation from chloroform/petroleum spirit mixture did not improve the purity of the product. A precipitate was not obtained at the addition stage with TFA$^-$ but needle-like crystals of the required compound formed on setting aside the reaction mixture overnight.

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Table I.

Systematic name	Trivial name	Abbreviation used
1,3-diphenyl-1,3-propanedione	dibenzoyl methane	HDBM
2,4-pentanedione	acetylacetone	HAA
1,1,1-trifluoro-4-(2-thienyl)-2,4-butanedione	thenoyltrifluoroacetone	HTTA
1-phenyl-1,3-butanedione	benzoylacetone	HBA
1,1,1-trifluoro-4-phenyl-2,4-butanedione	benzoyltrifluoroacetone	HBTA
1,1,1-trifluoro-2,4-pentanedione	trifluoroacetylacetone	HTFA
1,1,1,5,5,5-hexafluoro-2,4-pentanedione	hexafluoroacetylacetone	HHFA

An oil separated from europium solutions during addition of NaHFA and it failed to yield a crystalline product overnight. The oil was taken up in ether, the extract dried and the ether removed by distillation. The residual oil was extracted twice with 10 ml portions of boiling *n*–hexane which yielded the crystalline tris product on cooling.

Eu(AA)$_3$. 3H$_2$O. This substance was prepared by the method of Stites *et al.*[10] in 30% yield. A better yield (60%) was however obtained by the following simpler method which does not require constant pH adjustment. Methanol (10 ml) containing hydrated europium(III) nitrate (0.5 mmole) and HAA (3 mmole) was saturated with ammonia from heated aqueous ammonia (S.G. 0.88) solution.

The resulting yellow solution was evaporated under reduced pressure to near dryness. The residual yellow oil and crystals were washed with several portions of water. The white crystals remaining were dried in air; the product should not require recrystallisation.

Eu(TTA)$_3$. 2H$_2$O. The method of Charles and Ohlmann[11] was employed except that the recrystallisation step was omitted and the 'crude' product was stirred rather longer by way of compensation with *n*–pentane.

Tetrakis Diketonates

Alkali Metal Salts of [Eu(DBM)$_4$]$^-$. The method of Melby *et al.*[5] was used to obtain the potassium and sodium salts.

Piperidinium (PIP) Salts of [Eu(DBM)$_4$]$^-$, [Eu-(TTA)$_4$]$^-$, [Eu(BA)$_4$]$^-$, [Eu(BTA)$_4$]$^-$, [Eu(TFA)$_4$]$^-$, and [Eu(HFA)$_4$]$^-$. The method described by Whan and Crosby[6] was adapted for the preparation of the piperidinium salts of all these tetrakis complexes of europium. Europium(III) chloride (2 mmole) in ethanol (10 ml) was added dropwise to the diketone (8 mmole) and piperidine (8 mmole) in ethanol. The final volume of ethanol and the subsequent isolation of the tetrakis complex depended on the diketone used.

The product from HDBM readily precipitated from solution; the mixture (160 ml) was reduced in volume by evaporation under reduced pressure to about 100 ml and the solid separated by filtration and dried in air.

Precipitates were not obtained from ethanol solutions (60 ml) containing TTA$^-$, BA$^-$, or BTA$^-$. The solutions were reduced in volume by evaporation under reduced pressure using the minimum of heat until crystallisation commenced. After cooling in an ice/salt mixture the well-formed crystals thus obtained were removed by filtration and air dried. Elemental analyses were satisfactory and recrystallisation was thus considered unnecessary.

For the remaining two diketonate systems complete removal of the ethanol (40 ml) gave rise only to viscous brown oils interspersed with crystals probably of piperidinium chloride. Extraction of each with acetone (25 ml) served to effect a separation from the last mentioned salt. Removal of the acetone gave brown oils.

[Eu(HFA)$_4$]PIP remained as a white residue on treatment of the appropriate oily residue with cold *n*–pentane; [Eu(TFA)$_4$]PIP was only obtained as a rather impure brown product by this procedure.

Results and Discussion

The results from elemental analyses of a selection of tris and tetrakis europium(III) diketonates prepared as described in the previous section are presented in Table II. Yields are also given in the table and it will be seen that they are quite variable, ranging from around 20% to near 100% with reference to the europium salt used in the preparation.

At present there is a lack of quantitative thermodynamic and other data of use in planning preparative schemes for substances of the classes under consideration. For a particular synthesis the chemist is therefore obliged to fall back on general qualitative factors and observations. In this connection it is generally recognised that a ratio of diketone: base: europium(III) of 3: 3: 1 favours tris and a ratio 4: 4: 1 tetrakis complexes. However, this only provides a rough guide to ratios of reactants to be mixed and it does not necessarily lead to the desired product or, if it is obtained, to a satisfactory yield. This is well-illustrated by reference to europium dibenzoylmethide complexes. The method of Melby *et al.*[5] using a 4: 4: 1 ratio gives complexes such as [Eu(DBM)$_4$]K in good yield; a 5: 3: 1 ratio in the presence of ammonia has been reported[12] to give Eu(DBM)$_3$. H$_2$O and a 3: 3: 1 ratio with sodium hydroxide as base gives[9] a basic product consistent with the formula Eu$_2$(DBM)$_5$OH (see also Table II).

The method of Whan and Crosby[6] was found to

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[10] J.G. Stites, C.N. McCarty, and L.J. Quill, *J. Am. Chem. Soc.*, *70*, 3142 (1948).

[11] R.G. Charles and R.C. Ohlmann, *J. Inorg. Nucl. Chem.*, *27*, 255 (1965).

[12] R.G. Charles and A. Perotto, *J. Inorg. Nucl. Chem.*, *26* 373 (1964).

Table II. Characterisation and yields for the europium complexes.

	Carbon		Hydrogen		Nitrogen		Percentage	Refs. to previous
	Found	Required	Found	Required	Found	Required	yield [a]	work
$Eu(DBM)_3$	65.7	65.8	4.29	4.02			100 [b]	6,7,12,16,17
$Eu_2(DBM)_5OH$	62.2	62.7	3.87	3.90			70	9
$Eu(AA)_3 . 3H_2O$	35.9	35.8	5.41	5.37			60	p.w.
$Eu(AA)_3 . 3H_2O$ [d]	36.0	35.8	5.38	5.37			30	7,8,10,16
$Eu(TTA)_3 . 2H_2O$	35.6	33.8	2.44	1.88			40	7,11,16
$Eu(BA)_3 . 2H_2O$	53.5	53.7	4.32	4.62			50	7,16
$Eu(BTA)_3 . 2H_2O$	43.7	43.2	2.56	2.64			60	7,9,16
$Eu(TFA)_3 . 2H_2O$	27.6	27.8	2.47	2.47			20	7
$Eu(HFA)_3 . 2H_2O$	24.0	22.3	0.79	0.87			30	18,19,24
$[Eu(DBM)_4]PIP$ [c]	69.0	69.0	4.93	4.96	1.27	1.24	70	4,5,6,8
$[Eu(TTA)_4]PIP$	39.7	39.6	1.82	2.50	1.46	1.25	50	4
$[Eu(BA)_4]PIP$	61.1	61.2	5.45	5.44	1.58	1.59	40	5,6,8
$[Eu(BTA)_4]PIP$	49.1	49.2	3.29	3.28	1.25	1.28	60	8
$[Eu(TFA)_4]PIP$	35.8	35.3	3.46	3.29	2.12	1.65	40	8
$[Eu(HFA)_4]PIP$	28.3	28.1	1.50	1.50	1.36	1.31	30	24
$[Eu(DBM)_4]Na . H_2O$	66.1	66.4	5.27	4.24			40	5
$[Eu(DBM)_4]K$	66.6	66.5	3.79	4.06			60	5

[a] Yields are calculated relative to the quantity of europium salt added to the reaction mixture. [b] Yield based on the quantity of $[Eu(DBM)_4]PIP$ used. [c] % europium: found, 13.54; required: 13.55. [d] By the method of Stites et al.[10].

work satisfactorily in the preparation of piperidinium tetrakis complexes when applied to most of the diketones listed in Table I. Having due regard to differences in solubility of the various complexes (see experimental section) good yields of reasonably pure products are obtained (Table II). By virtue of the procedure adopted, hydrated tetrakis diketonates of the type reported by Workman and Burns[13] are not observed.

Suitable tetrakis diketonates can be converted by thermal decomposition to the corresponding anhydrous tris compounds in good yield. The choice of base used in the preparation has an overall bearing on the success of this reaction sequence. It should be of sufficient strength to lead to adequate ionisation of the diketone for tetrakis formation. Thus iso-quinoline ($K_B = 2.5 \times 10^{-9}$) is unsatisfactory[14] when the diketone is a weak acid like HDBM but piperidine ($K_B = 1.6 \times 10^{-3}$) works well (see Table II). The adduct between the diketone and base should possess adequate thermal stability and volatility, *e.g.* PIP . TTA,[15] to facilitate its displacement from the desired reaction product in the thermal decomposition. Cation size and polarisability have important effects on lattice energy and the polarisability will also influence adduct stability in the vapour phase. It is therefore to be expected that cations like PIP will be superior to those of the alkali metals which have also been used[16] for this purpose.

Anhydrous diketonates can also be prepared starting from anhydrous europium chloride or the isopropoxide[17] and water-free solvents but unless such substances are to hand times taken over the preparations are lengthened. If water is not exluded from the solvents, the tris diketonates are invariably hydrated;[5,11,12,18,19] occasionally tetrakis complexes will be hygroscopic as for example where light alkali metal bases are used as in $[Eu(DBM)_4]Na$ (see Table II). (Hydrated tris complexes, in favourable cases[7] can be converted thermally to anhydrous forms). In general, however, it would appear that tetrakis diketonates are more readily isolated from solution in a single stoichiometric form than the corresponding tris complexes. This is at least partly due to the tendency of the latter to retain solvent, paricularly water, to increase the coordination number of the europium(III). Problems may then be encountered in attempting to improve the purity of the product by recrystallisation.[20] When hydrocarbons are otherwise the best solvents, dissolution and subsequent precipitation may be slow if water has to be recovered from the atmosphere. Slow recovery from solution leaves the dissolved substance susceptible to decomposition, *e.g.* by ligand rearrangement or oxidation. Attempts to further purify $Eu(BA)_3 . 2H_2O$ by recrystallisation from chloroform/petroleum spirit illustrate the problem. Two successive batches of crystals from this solvent mixture gave progressively poorer analysis figures for the products assuming the dihydrate formulation. Hydrolytic reactions may also participate, in which case diketones of high basicity in the Lewis sense, *i.e.* HAA and HBA rather than HBTA or HHFA give rise to complexes most likely to be affected in this way. The difficulties referred to here can be alleviated or overcome by working in an inert atmosphere or by addition of some free diketone to the solvent prior to dissolution of the complex.[21] It is, of course, more convenient to be able to devise for use a method which avoids the need for a recrystallisation. However, this is not always readily accomplished as for example the procedure adapted in the present work for the preparation of $Eu(TTA)_3 . 2H_2O$ illustrates. The product obtained contained coprecipitated HTTA and

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(13) M.O. Workman and J.H. Burns, *Inorg. Chem.*, *8*, 1542 (1969).

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(16) Y. Matsuda, S. Makishima, and S. Shionoya, *Bull. Chem. Soc. Jap.*, *42*, 356 (1969).

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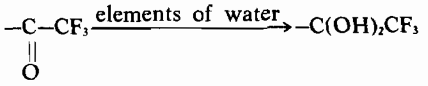
(21) G.W. Pope, J.F. Steinbach, and W.F. Wagner, *J. Inorg. Nucl. Chem.*, *20*, 304 (1961).

it is in this instance advisable to follow the method of Charles and Ohlmann[11] closely.

Some difficulty was experienced in the isolation of tetrakis complexes from fluorinated diketones particularly HTFA and HHFA. Reaction mixtures give rise to viscous oils in which the metal complexes and piperidinium chloride are in solution or admixture. Differential solution in suitable solvents is required to effect isolation of the metal complex. (Because of the 'labile' nature of diketone complexes of lanthanides, column chromatography is not in general a suitable alternative method of purification in our experience.) The oily biproducts undoubtedly arise from side reactions involving the ligand. Hydrolysis of fluorine on trifluoromethyl groups does not appear to be responsible since fluoride ion is absent from the reaction mixture. Break-up of the ligand could occur at the carbon atom situated between the carbonyl groups. It would not be difficult to postulate free radical induced polymerisations initiated at such a centre to explain the observed phenomenon. It is also possible that 'addition' of water, as has been postulated[22] for the 'hydrate' of HTTA, occurs along the lines



$$-\underset{\underset{\displaystyle O}{\|}}{C}-CF_3 \xrightarrow{\text{elements of water}} -C(OH)_2CF_3$$

giving a carbon atom susceptible to attack by nucleophiles. Hydroxyl ion attack would give rise to the trifluoroacetate ion which has been found[23] as a ligand in metal complexes isolated from such systems.

It is seen from the preceding discusion that a number of factors determine the ease or otherwise with which the desired metal diketonate may be obtained. The outcome of a reaction will depend on the thermodynamic stability of one species of metal complex relative to others, molar ratios and the order of mixing of reactants, solvents, hydrogen ion activity and the vulnerability of ligand species to competitive side reactions.

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