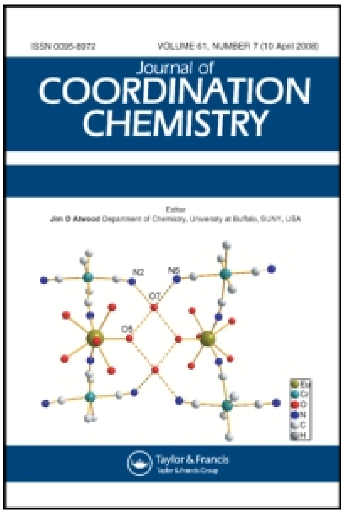

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Sergto Sttran[a]; Dolores Fregona[a]; Giuseppina Faraglia[b]
[a] Istituto di Chimica e Tecnologia dei Radioelementi del C. N. R., Padova, Italy [b] Dipartimento di Chimica Inorganica, Metallorganica ed Analilica dell'Universita, Padova, Italy

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LANTHANIDE COMPLEXES OF 2,6-DIFORMYL-4-METHYLPHENOL

SERGIO SITRAN,* DOLORES FREGONA

Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., corso Stati Uniti, 35020 Padova, Italy

and GIUSEPPINA FARAGLIA

Dipartimento di Chimica Inorganica, Metallorganica ed Analitica dell'Università, via Loredan 4, 35100 Padova, Italy

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The reaction of 2,6-diformyl-4-methylphenol H(MDA), with lanthanide(III) acetate in aqueous methanol generally yields complexes of formula $[M(MDA)_3]$, except for lanthanum, which forms the mixed adduct $[La(MDA)_2(O_2CMe)].H(MDA)$. The last compound releases the neutral ligand molecule on heating, yielding the anhydrous species $[La(MDA)_2(O_2CMe)]$. For M = Ce, either the main product $[Ce(MDA)_3]$ or a small amount of the mixed complex $[Ce(MDA)_2(O_2CMe)]$ has been isolated. The complexes have been characterized by infrared, ^1H and ^{13}C nmr spectroscopy and by thermogravimetric measurements.

Keywords: Lanthanides, diformylphenols, acetals, complexes, thermal behaviour

INTRODUCTION

Recently we reported the behaviour of the ligands 2,6-diformyl-4-chlorophenol, H(DIAL), and 2,6-diformyl-4-methylphenol, H(MDA), and of the related uranyl complexes $[UO_2(L)_2(L^i)]$ (L = DIAL or MDA; L^i = H_2O, MeOH or EtOH) in alcoholic media.[1-3] In particular we observed than either free or coordinated dialdehydes undergo acetalation of one of the formyl groups in boiling methanol and ethanol. As regards H(MDA), the acetalated species 2-dimethylacetal-4-methyl-6-formylphenol, H(MAC), and the diethylacetal analogue, H(EAC), have been isolated and characterized along with the uranyl complexes $[UO_2(MAC)_2(MeOH)]$ and $[UO_2(EAC)_2]$. When those complexes were treated with diamines, the condensation reaction involved the residual formyl group of the ligand molecule, the acetalated group being unchanged.[3-5] Consequently, acetalated species should be expected to form, totally or in part, when template syntheses of Schiff base complexes are carried out in alcohols. As an example, reaction of praseodymium(III) nitrate with H(MDA) in the presence of triethylenetetramine was found to yield a 1:1 complex containing the acetalated anion $\{(CH_3O)_2CH\text{–}OC_6H_2CH_3\text{–}HC{=}N[(CH_2)_2NH]_2\text{–}(CH_2)_2NH_2\}^-$.[6] Moreover in an attempt to synthesize lanthanide Schiff base complexes by H(MDA)-amine condensation in the presence of metal salt, we obtained solid products containing variable amounts of acetalated functions.

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* Author for correspondence

Because of diformylphenol versatility it was thought worthwhile to examine, step by step, the lanthanide salt–H(MDA) system in various media. Accordingly, this paper reports a study on the interaction of H(MDA) with lanthanide(III) acetates in aqueous methanol.

EXPERIMENTAL

Chemicals

Hydrated lanthanide(III) acetates (J. Matthey) were used as supplied. Water content in each sample was estimated by thermal analysis. The ligand 2,6-diformyl-4-methylphenol (H(MDA), $C_9H_8O_3$) was prepared and purified as reported in ref. 5. Deuterated dimethyl sulfoxide (d_6-DMSO) was kept over molecular sieves.

Preparation of the Compounds

$[La(MDA)_2(O_2CMe)].H(MDA)$

A methanol solution of H(MDA) (3.0 mmol in 25 cm^3) was added to an aqueous solution of lanthanum triacetate (1.0 mmol in 20 cm^3). The yellow solution gradually deposited (12 h) a bright yellow powder. The product was separated by centrifugation, washed with *n*-pentane and dried *in vacuo*. Yield, 70%. Found: C, 50.1; H, 3.6%. Calcd. for $C_{29}H_{25}LaO_{11}$: C, 50.6; H, 3.6%. Further fractions of the complex were obtained by slow evaporation of the supernatant.

$[La(MDA)_2(O_2CMe)]$

This complex was obtained by heating the H(MDA) adduct (above) in the thermoanalyzer to 235° C (alumina crucible). The sample was removed and cooled in a desiccator over P_2O_5. Found: C, 46.2; H, 3.2%. Calcd. for $C_{20}H_{17}LaO_8$: C, 45.8; H, 3.2%.

$[M(MDA)_3]$

The complexes (M = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb) were obtained with 70–80% yields as bright yellow powders (except for [Ce(MDA)$_3$], ochre, yield *ca* 50%). As a general method, a methanol solution of H(MDA) (3.6 mmol in 30 cm^3) was added to an aqueous solution of the appropriate lanthanide acetate (1.2 mmol in 25 cm^3). The resulting yellow solution deposited the sparingly soluble complex in a few minutes. After centrifugation the solid was washed with *n*-pentane and dried *in vacuo*. Elemental analysis results for the complexes (calculated values for $C_{27}H_{21}MO_9$ in parentheses) were: [Ce(MDA)$_3$]: C, 50.9; H, 3.3% (C, 51.5; H, 3.4%); [Pr(MDA)$_3$]: C, 50.9; H, 3.3% (C, 51.4; H, 3.4%); [Nd(MDA)$_3$]: C, 50.8; H, 3.3% (C, 51.2; H, 3.3%); [Sm(MDA)$_3$]: C, 50.2; H, 3.2% (C, 50.7; H, 3.3%); [Eu(MDA)$_3$]: C, 50.2; H, 3.3% (C, 50.6; H, 3.3%); [Gd(MDA)$_3$]: C, 50.1; H, 3.4% (C, 50.1; H, 3.2%); [Tb(MDA)$_3$]: C, 49.7; H, 3.2% (C, 50.0; H, 3.3%); [Dy(MDA)$_3$]: C, 49.5; H, 3.3% (C, 49.7; H, 3.2%); [Ho(MDA)$_3$]: C, 49.2; H, 3.3% (C, 49.5; H, 3.2%); [Er(MDA)$_3$]: C, 48.9; H, 3.2% (C, 49.4; H, 3.2%); [Yb(MDA)$_3$]: C, 48.4; H, 3.2% (C, 48.9; H, 3.2%).

[Ce(MDA)$_2$(O$_2$CMe)]

The compound precipitated slowly from the deep yellow supernatant from the [Ce(MDA)$_3$] preparation, which was left standing in air for a few days. The ochre solid was separated by centrifugation, washed with *n*-pentane and dried *in vacuo*. Yield, 15%. Found: C, 46.1; H, 3.3%. Calcd. for $C_{20}H_{17}CeO_8$: C, 45.7; H, 3.2%.

Measurements

Infrared spectra were obtained using a Perkin-Elmer 580B spectrophotometer (4000–400 cm^{-1}; KBr pellets). ^{1}H nmr spectra ($\leqslant$8 mg in 0.5 cm^3 d_6-DMSO) and ^{13}C nmr spectra (15 mg in 0.5 cm^3 d_6-DMSO) were obtained with a Jeol FX 90 Q spectrometer. Thermogravimetric data (TG and DTA) in air were obtained using a Netzsch STA-429 thermoanalytical instrument (air flux rate, 250 cm^3 min^{-1}; heating rate, 5° C min^{-1}; reference material Al_2O_3).

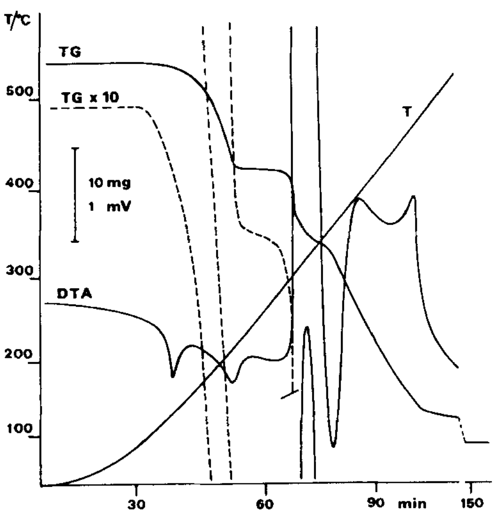

FIGURE 1 Thermograms of [La(MDA)$_2$(O$_2$CMe)].H(MDA) (52.43 mg).

RESULT AND DISCUSSION

The reaction of H(MDA) with the appropriate lanthanide acetate (molar ratio 3:1) in aqueous methanol yields complexes of general formula [M(MDA)$_3$] except for lanthanum, which retains one of the acetate groups to form the compound [La(MDA)$_2$(O$_2$CMe)].H(MDA). In the last compound the weakly bonded molecule of neutral ligand is easily released by gentle heating under reduced pressure. The thermograms in air (Figure 1, Table I) show a first decomposition step which follows the melting process (130° C). The weight loss is consistent with evolution of one H(MDA) molecule to form [La(MDA)$_2$(O$_2$CMe)] as an intermediate, which is stable up to 280° C. The pyrolysis of the intermediate is strongly exothermic (DTA peaks at

TABLE I
Thermal decomposition data for the complexes (in air).

Compound	Decomposition interval (° C)	TG weight loss %	
		Found	Calcd.[a]
$[La(MDA)_2(O_2CMe)].H(MDA)$	90–220	21.6	23.8[b]
	280–800	55.8	52.5
$[La(MDA)_2(O_2CMe)]$	280–800	72.1	68.9
$[Ce(MDA)_3]$	280–480	73.5	73.9
$[Pr(MDA)_3]$	310–590	73.1	73.8[c]
$[Nd(MDA)_3]$	280–680	73.5	73.4
$[Sm(MDA)_3]$	280–660	73.2	72.7
$[Eu(MDA)_3]$	300–660	73.3	72.7
$[Gd(MDA)_3]$	310–600	73.1	72.0
$[Tb(MDA)_3]$	320–580	72.5	71.8
$[Dy(MDA)_3]$	315–590	71.3	71.4
$[Ho(MDA)_3]$	335–590	71.1	71.2
$[Er(MDA)_3]$	320–590	71.0	70.8
$[Yb(MDA)_3]$	315–590	71.6	70.2

[a] For M_2O_3 as final degradation product. [b] For the release of the H(MDA) molecule; DTA peak, 215° C. [c] For Pr_6O_{11} as final product.

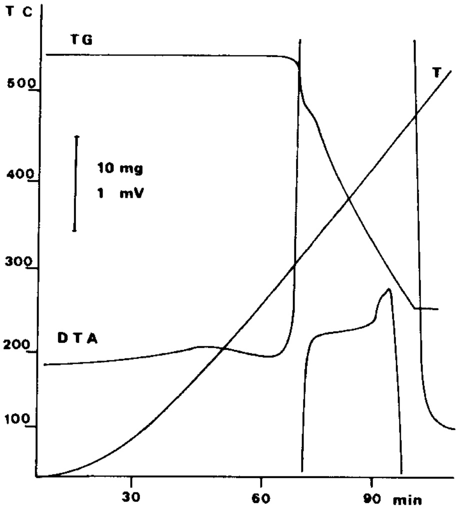

FIGURE 2 Thermograms of $[Ce(MDA)_3]$ (36.5 mg).

328°, 392° and 479° C) and the major weight loss occurs in the 280–490° C temperature interval. Successively, a slow degradation process is observed, which ends at *ca* 800° C (weight loss, *ca* 5%). When left standing in air for several days, the intermediate does not bind water molecules, as tested by repeated thermal analyses. The thermograms of the complexes of formula $[M(MDA)_3]$ (Table I) resemble those of [Ce(MDA)$_3$] (Figure 2), which decomposes in a single step to give Ce_2O_3. The thermal data confirm the absence of water in all complexes. Lanthanide acetylacetonates[7-10] and benzoates,[11] which are coordinatively non-saturated and consequently can bind neutral ligands, have been found to release coordinated and outer-sphere water molecules in the 90–200° C temperature range. When the residual solution from the [Ce(MDA)$_3$] preparation is allowed to evaporate in air, the mixed anhydrous complex [Ce(MDA)$_2$(O_2CMe)] precipitates, which does not contain any additional H(MDA) (or H_2O) molecule. Under similar conditions the mother solutions of some lanthanides separate solid samples which contain non-stoichiometric amounts of acetate and, in case, of H(MDA).

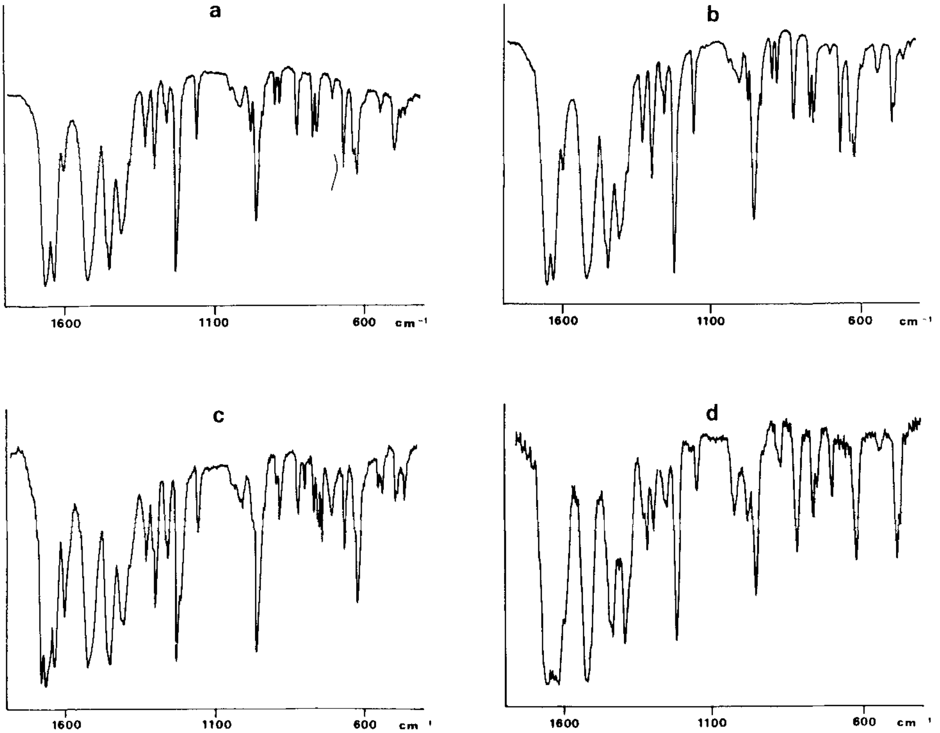

FIGURE 3 Infrared spectra of *a*: [La(MDA)$_2$(O_2CMe)]; *b*: [Ce(MDA)$_2$(O_2CMe)]; *c*: [La(MDA)$_2$(O_2CMe)].H(MDA); *d*: [Ce(MDA)$_3$].

The infrared spectrum of H(MDA) contains two strong bands, at 1685 cm^{-1} and 1670 cm^{-1}, due to vibration of the free C=O group and of the C=O group bonded to hydroxyl by an intramolecular bond, respectively.[5] In coordinated MDA anion the chelated formyl group (C=O) is observed at *ca* 1640 cm^{-1}, in accordance with the corresponding absorption in acetalated complexes. As is shown in Figure 3, the mixed complexes [M(MDA)$_2$(O_2CMe)] (M = La or Ce) have almost identical infrared spectra, in which the absorption at *ca* 1639 cm^{-1} is of the chelated carbonyl and the one at 1666 cm^{-1} is due to the unchelated formyl group. The shift to lower energy with respect to free carbonyl supports intermolecular coordination to form

TABLE II

Significant infrared frequencies (cm^{-1}) for the complexes.

Compound	1700–1450 cm^{-1} region							
[$La(MDA)_2(O_2CMe)$].H(MDA)	1685vs	1670vs		1641vs		1607m	1526s	1454
[$La(MDA)_2(O_2CMe)$]		1667vs		1638vs			1526vs	1454
[$Ce(MDA)_2(O_2CMe)$]		1665vs		1640vs			1528vs	1453
[$Ce(MDA)_3$]		1666vs	1658vs	1644vs	1628vs	1609m	1532vs	1447
[$Pr(MDA)_3$]		1666vs	1658vs	1644vs	1626vs	1609m	1534vs	1447
[$Nd(MDA)_3$]		1667vs	1658vs	1635s	1626vs	1609m	1534vs	1447
[$Sm(MDA)_3$]		1670vs	1653s	1633vs		1611m	1534vs	1450
[$Eu(MDA)_3$]		1670vs	1655s	1632vs		1610m	1535vs	1450
[$Gd(MDA)_3$]		1671vs	1652s	1634vs		1610m	1536vs	1450
[$Tb(MDA)_3$]		1670vs	1651s	1634vs		1609m	1535vs	1453
[$Dy(MDA)_3$]		1672vs	1650s	1635vs		1609m	1537vs	1455
[$Ho(MDA)_3$]		1670vs	1652vs	1635vs		1609m	1537vs	1454
[$Er(MDA)_3$]		1671vs	1653s	1635vs		1609m	1534vs	1456
[$Yb(MDA)_3$]		1673vs	1654s	1636vs		1610w	1538vs	1457

polymeric species. The additional H(MDA) molecule in $[La(MDA)_2(O_2CMe)]$.H(MDA) is clearly identified by the strong band at 1685 cm^{-1} (Figure 3c), which suggests that the H(MDA)-mixed complex interaction occurs through the hydrogen bonded group of the neutral molecule. The presence of three coordinated MDA anions causes an increased band multiplicity in the 1620–1700 cm^{-1} region (Table II). In fact, the complexes $[M(MDA)_3]$, in which M = Ce, Pr and Nd, show two strong doublets, at 1666–1658 cm^{-1} and 1644–1628 cm^{-1}, whereas for the heavier lanthanides the lower energy absorption is at *ca* 1635 cm^{-1}. All complexes present a strong band at *ca* 1535 cm^{-1}, associated with the coordinated phenolato anion, and a weak absorption at *ca* 2835 cm^{-1} due to stretching of the MDACH bonds. The formation of mixed species can be inferred by the spectral trend in the 600–700 cm^{-1} range. In this region all 1:3 complexes present a band of medium intensity at *ca* 638 cm^{-1}, whereas the mixed species show two medium bands at 629 cm^{-1} (641 (sh) cm^{-1}) and 675 cm^{-1}, the last one characteristic of the acetato group.

TABLE III

^{1}H nmr data for the complexes (d_6-DMSO; ppm; T *ca* 27° C).

Compound	CH_3	CH_{ring}	CH_{formyl}	other
H(MDA)[a]	2.33	7.87	10.20	11.39[b]
$[UO_2(MDA)_2(MeOH)]$[a]	2.37	7.88	10.72	3.16, 4.05[c]
$[La(MDA)_2(O_2CMe)]$.H(MDA)	2.15	7.49	10.01	11.9[b], 1.86[d]
$[La(MDA)_2(O_2CMe)]$	2.14	7.47	10.00	1.72[d]
$[Ce(MDA)_2(O_2CMe)]$	3.26	9.50	13.30	2.90[d]
$[Ce(MDA)_3]$	3.22	9.49	13.35	
$[Pr(MDA)_3]$	4.89	12.41	18.5	
$[Nd(MDA)_3]$	3.53	10.18	15.85	
$[Sm(MDA)_3]$	2.33	7.83	10.05	
$[Eu(MDA)_3$	0.57	0.57[e]	4.36[e]	
$[Tb(MDA)_3]$[f]	23.6	23.6[e]	42.0[e]	
$[Dy(MDA)_3]$[f]	29.9	29.9[e]	52.3[e]	
$[Ho(MDA)_3]$[f]	14.8	19.8[e]	28.5[e]	
$[Er(MDA)_3]$[f]	−3.7	−3.7[e]	1.1[e]	
$[Yb(MDA)_3]$[f]	−5.3	−3.2[e]	−0.8[e]	

[a] From ref. 5. [b] Phenolic proton. [c] MeOH protons. [d] Acetato group protons. [e] Tentative assingment. [f] Very broad.

The ^{1}H nmr spectra of the complexes in deuterated dimethyl sulphoxide (Table III) show equivalent proton signals spread over a wide range, owing to the different magnetic properties of the metal ions. The H(MDA) spectrum consists of four singlets, related to each group of equivalent protons. The two formyl groups are equivalent in solution, owing to intermolecular OH proton exchange. In the MDA uranyl complexes a downfield shift of the formyl proton resonance was observed (*ca* 0.5 ppm). Conversely in lanthanum complexes, all MDA signals shift upfield with respect to the corresponding ones in H(MDA), and the acetato proton singlet is at *ca* 1.8 ppm. In the H(MDA) adduct the additional neutral ligand is identified by the presence of the phenolic OH signal at 11.9 ppm. Whereas the proton nmr spectrum of the [La(MDA)$_2$(O$_2$CMe)] d_6-DMSO solution is unchanged over several days, the H(MDA) adduct solution undergoes a progressive decrease of signal at 11.9 ppm, suggesting slow exchange of the neutral ligand with the acetato group in solution. Such a reaction can probably occur in the solid state as well. In fact, solid samples of [La(MDA)$_2$(O$_2$CMe)].H(MDA), tested by proton nmr and thermal analysis, contain after *ca* one month 60% of the initial H(MDA), with a parallel decrease of acetate. Some acetate–MDA exchange on heating could account for the weight loss on the first decomposition step of the adduct, which was lower than the calculated value for release of one H(MDA) molecule (21.6% against 23.8%) and for the elemental analysis data for [La(MDA)$_2$(O$_2$CMe)]. The proton nmr spectra of the Ce, Pr, Nd and Sm complexes contain well-resolved singlets, whereas important line broadening is observed for the heavier lanthanide complexes, especially for Ho, Er and Yb derivatives. Except for Eu, Er and Yb, the proton group signals are shifted downfield with respect to the corresponding signals in H(MDA) and in some cases the methyl proton resonances are superimposed on one of the signals of area 2H (Eu, Tb and Dy). Excessive broadening causes the spectrum of the gadolinium complex to be uninterpretable. Along with the formyl and methyl carbon signals (192.1 ppm and 19.4 ppm respectively), the ^{13}C nmr spectrum of H(MDA) shows four ring carbon signals, the one at 160.2 ppm belonging to the phenolato carbon (Table IV). In the [UO$_2$(MDA)$_2$(MeOH)] spectrum the formyl (192.4 ppm) and methyl (19.5 ppm) carbon resonances were unchanged with respect to H(MDA), whereas the phenolato carbon resonance experienced a noticeable downfield shift (173.8 ppm).[5] A parallel behaviour is observed for the MDA ligand in [La(MDA)$_2$(O$_2$CMe)], in which the acetato group is identified by the resonances at 24.5 ppm (CH$_3$) and 191.1 ppm (–CO$_2$). Metal paramagnetism slightly alters the MDA formyl and methyl carbon signals, which show small downfield shifts with respect to lanthanum. As regards ring carbon atoms, the phenolato carbon resonance is absent in the Ce, Pr, Nd and Eu spectra, probably owing to broadening. It was impossible to measure ^{13}C nmr spectra for lanthanides heavier than gadolinium, owing to the low solubility of the MDA complexes in d_6-DMSO.

TABLE IV
^{13}C nmr data for the complexes (d_6-DMSO; ppm; T *ca* 27° C).

Compound	COH	CH$_{ring}$	CH$_3$	CH$_3$CO$_2$	CH$_3$CO$_2$
[La(MDA)$_2$(O$_2$CMe)]	191.8	171.7, 138.2, 127.1, 120.1	19.5	24.5	191.1
[Ce(MDA)$_2$(O$_2$CMe)]	193.0	140.7, 137.2, 123.3	20.5	31.7	191.4
[Ce(MDA)$_3$]	192.8	141.0, 137.1, 123.3	20.4		
[Pr(MDA)$_3$]	195.6	152.5, 145.6, 127.6	22.2		
[Nd(MDA)$_3$]	193.4	147.0, 142.5, 125.0	20.9		
[Sm(MDA)$_3$]	192.7	174.5, 139.8, 127.4, 121.2	19.7		
[Eu(MDA)$_3$]	195.8	136.1, 116.6	18.6		
H(MDA)[a]	192.1	160.2, 137.2, 129.1, 123.1	19.4		

[a] Ref. 5.

REFERENCES

1. S. Sitran, D. Fregona, U. Casellato, P.A. Vigato and G. Faraglia, *J. Coord. Chem.*, **15**, 173 (1986).

2. S. Sitran, D. Fregona, U. Casellato, P.A. Vigato R. Graziani and G. Faraglia, *Inorg. Chim. Acta*, **121**, 103 (1986).
3. S. Sitran, D. Fregona and G. Faraglia, *J. Coord. Chem.*, **16**, 395 (1988).
4. S. Sitran, D. Fregona, U. Casellato, P.A. Vigato R. Graziani and G. Faraglia, *Inorg. Chim. Acta*, **132**, 279 (1987).
5. S. Sitran, D. Fregona and G. Faraglia, *J. Coord. Chem.*, **16**, 293 (1987).
6. I.A. Kahwa, F.R. Fronczek and J. Selbin, *Inorg. Chim. Acta*, **126**, 227 (1987).
7. L.I. Martynenko, I.A. Murav'eva, N.H. Khalmurzaev and D.I. Spitsyn, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 449 (1984).
8. G.V. Trembovetskii, L.I. Martynenko, N.A. Murav'eva and V.I. Spitsyn, *Dokl. Chem. (Engl. Transl.)*, **277**, 273 (1984).
9. N.G. Dzyubenko and L.I. Martynenko, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **31**, 973 (1986).
10. G.I. Gerasimenko and H.S. Poluektov, *Dokl. Chem. (Engl. Transl.)*, **278**, 283 (1984).
11. G.N. Makushova and S.B. Pirkes, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **29**, 531 (1984).