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CHROMATE AND CHROMATE–DICHROMATE COMPLEXES OF LANTHANIDE-CONTAINING MACROCYCLES

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Abstract—Anion metathesis between aqueous K_2CrO_4 and the $[ML(CH_3COO)_2]Cl$ complexes, where M is a lanthanide(III) ion and L is the six-nitrogen-donor macrocyclic ligand $C_{22}H_{26}N_6$, produced a series of crystalline chromate-containing species, the stoichiometry and structure of which depended on the size of the metal centre. The larger lanthanides, La^{III}–Nd^{III}, gave yellow, water-insoluble complexes of formula $ML(CrO_4)_{1.5} \cdot 5H_2O$, containing only ionic chromate. The Ce^{III} analogue was oxidized to $CeL(CrO_4)_2 \cdot 6H_2O$, also insoluble and containing only ionic chromate. The smaller lanthanides, Er^{III}–Lu^{III}, gave extremely soluble yellow products which were not isolated as analytically pure chromate-only species. The intermediate lanthanides gave two series of complexes, the yellow $[(CrO_4)LM(\mu CrO_4)ML(CrO_4)] \cdot nH_2O$ (M = Sm–Ho, n = 10 or 11), containing chelating as well as bridging chromate, and the photochromic (golden → red-brown) $[ML(CrO_4)(H_2O)]_2(Cr_2O_7) \cdot 2H_2O$ (M = Sm–Gd), containing chelating chromate and ionic dichromate. In both series the L macrocycle functions as a hexadentate ligand and the lanthanide(III) is 9-coordinate. The chromate–dichromate complexes contain mononuclear coordination entities with bidentate chelating chromate; the chromate-only Eu^{III} complex contains dinuclear coordination entities with both chelating and bridging chromate ligands.

The coordination chemistry of the CrO_4^{2-} ion, unlike that of other tetrahedral oxonians (e.g. ClO_4^-, SO_4^{2-}), is relatively unknown. Only a few structures of metal complexes containing coordinated chromate have been reported[1,2] and for some of these the structural characterization was limited to IR spectroscopy.[2] This scarcity of metal–

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chromate complexes is most likely due to the low solubility of the 'simple' chromates of most metal ions (except those of Group IA), as well as to the oxidizing properties of Cr^{VI}. In general, the CrO_4^{2-} ion may be expected to function as a counterion or anionic ligand toward a $\{MX_y\}^{n+}$ complex moiety only when this is either extremely stable or substitution-inert. Furthermore, since the chromate ion can act as an oxidant toward many organic solvents, the precursors used in the synthesis of chromate complexes should be soluble in water or at least compatible with it.

The diacetate-chloride salts of the $\{ML\}^{3+}$ complex cations, in which M is a lanthanide ion, La^{III}–Lu^{III}, and L is the six-nitrogen-donor macrocyclic ligand $C_{22}H_{26}N_6$ shown in Fig. 1, satisfy these requirements.[3–6] The $[ML(CH_3COO)_2]Cl \cdot nH_2O$ complexes are very soluble in water. Their $\{ML\}^{3+}$ metal–macrocycle entities resist hydrolysis and are inert to metal release, even in the presence of those anions, such as hydroxide and oxalate, that are typical precipitating agents for the lanthanide(III) ions. In contrast, the exocyclic acetate ligands are labile and may be exchanged by other counterions.[4,5] This series of complexes therefore offers the opportunity to explore the coordination of CrO_4^{2-} to lanthanide(III) acceptors, in the absence of complications resulting from precipitation of simple chromate salts or oxidation of the organic ligands and solvent.

EXPERIMENTAL

Starting materials and procedures

The {ML} diacetate-chlorides were prepared as previously described.[3] Reagent grade potassium chromate and potassium dichromate (Aldrich) were used as received. Infrared spectra were recorded on a Perkin–Elmer 1600 FT-IR spectrophotometer, in the range 4000–400 cm^{-1}; samples were examined both as KBr pellets and as combinations of Nujol-hexachlorobutadiene mulls. No difference was observed between the two sets of IR spectra, showing that no reaction had occurred between the samples and KBr. Thermogravimetric analyses (TGA) were performed on a Perkin–Elmer thermogravimetric system TGS-2 under a dry He flow of 60 cm^3 min^{-1}. Powdery samples were examined for crystallinity with an ISI DS-130S scanning electron microscope. Microanalyses (C, H, N) were performed by Atlantic Microlab, Atlanta, Georgia; analytical data are presented in Table 1.

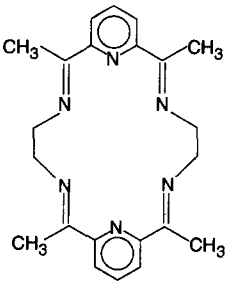

Fig. 1. Schematic formula of macrocyclic ligand: $L = C_{22}H_{26}N_6$.

Synthesis and characterization of the complexes

Chromate and chromate–dichromate complexes. A nearly saturated aqueous solution of $[ML(CH_3COO)_2]Cl \cdot nH_2O$ was filtered through a Millipore filter and mixed at room temperature with a nearly saturated, Millipore-filtered aqueous solution of K_2CrO_4. The CrO_4^{2-} to $\{ML\}^{3+}$ ratio was 1.5 : 1.0. Results and subsequent procedures varied with the metal centre.

The La^{III}, Ce^{III}, Pr^{III} and Nd^{III} species gave immediate precipitates (pale yellow, very small needles for La, Pr, Nd; golden brown fan-shaped clusters of needles for Ce); these were filtered with suction, washed first with water and then with acetone, and allowed to dry in air at room temperature. Yields were nearly quantitative. The compounds, $CeL(CrO_4)_2 \cdot 6H_3O$ and $ML(CrO_4)_{1.5} \cdot 5.5H_2O$ for M = La, Pr and Nd were practically insoluble in water and in most organic solvents. In the solid state, they lost water completely when heated in a dry atmosphere and rehydrated rapidly upon cooling in moist air. For the La^{III}, Pr^{III} and Nd^{III} species, TGA showed a single mass-loss step (45–100°C), with a slight inflection at 55°C, corresponding to the total loss of 5.5 H_2O. For the Ce^{IV} complex, three ill-defined steps were observed, corresponding to the loss of *ca* 2 H_2O (40–55°C), *ca* 3 H_2O (60–75°C), and *ca* 1 H_2O (80–110°C), respectively.

The Sm^{III}–Ho^{III} species gave a yellow solution from which small, well-formed bright yellow crystals began to separate after 5–30 min (Sm–Dy), or after concentration at room temperature (Ho). The products were filtered, washed first with a very small amount of ice-cold water and then with acetone, and dried; they had the empirical formula $ML(CrO_4)_{1.5} \cdot nH_2O$ ($n = 4$ for samples stored over Drierite, $n = 5$ for samples dried in air). Yields ranged from *ca* 60% for Sm to *ca* 10% for Ho. The yellow products were soluble in water and methanol, the solubility increasing markedly from Sm to Ho; the methanol solutions darkened with time.

Table 1. Analytical data and Cr—O stretching frequencies[a] of representative complexes

Complex	C(%)		H(%)		N(%)		Cr—O stretching frequencies (cm^{-1})
	Calc.	Found	Calc.	Found	Calc.	Found	
$LaL(CrO_4)_{1.5}\cdot 5.5H_2O$	33.6	33.8	4.7	4.7	10.7	10.6	895 vs; 878 sh; 860 sh
$CeL(CrO_4)_2\cdot 6H_2O$[b]	30.9	30.9	4.5	4.3	9.8	9.4	[Fig. 2(a)]
$PrL(CrO_4)_{1.5}\cdot 5.5H_2O$[c]	33.5	33.5	4.7	4.5	10.7	10.4	
$NdL(CrO_4)_{1.5}\cdot 5.5H_2O$	33.7	33.7	4.7	4.7	10.6	10.5	
$EuL(CrO_4)_{1.5}\cdot 4H_2O$	35.7	35.6	4.1	4.0	11.4	11.3	919 sh; 896 vs, br; 880 sh; 834–818[d]
$GdL(CrO_4)_{1.5}\cdot 4H_2O$	34.0	34.1	4.4	4.2	10.8	10.6	[Fig. 2(b)]
$DyL(CrO_4)_{1.5}\cdot 4H_2O$[e]	34.0	33.7	4.4	4.3	10.7	10.5	
$GdL(CrO_4)(Cr_2O_7)_{0.5}\cdot 0.5H_2O$[f]	33.8	33.7	3.9	3.7	10.7	10.6	926 vs, br; 898 vs; 877 sh; 839 m-s ;811 vs; 794 sh [Fig. 2(c)]
$LaL(Cr_2O_7)_{1.5}\cdot 1.5H_2O$	30.1	30.4	3.4	3.4	9.5	9.6	943 vvs; 906 s; 906 s; 877 m-s; 814 m-w; 787 vs [Fig. 2(d)]
$GdL(Cr_2O_7)_{1.5}\cdot 2H_2O$[g]	29.6	29.8	3.4	3.5	9.4	9.2	950 vvs; 931 vvs; 879 s; 818 vs[h]; 769 sh; 754 vs; 740 sh [Fig. 2(e)]

[a] Infrared spectra were obtained as KBr pellets and Nujol mulls. s, strong; m, medium; w, weak; sh, shoulder; v, very; br, broad.

[b] Weight loss to 135°C, 12.0%; calc. for $6H_2O$, 12.6%.

[c] Weight loss to 100°C, 12.8%; calc. for $5.5H_2O$, 12.6%.

[d] Partly resolved maxima of medium-strong band, overlapping with macrocycle absorption at 820 cm^{-1}.

[e] Weight loss to 150°C, 8.8%; calc. for $4H_2O$, 9.2%.

[f] The isostructural Sm and Eu complexes had identical IR spectra.

[g] The Eu and Dy analogues had identical IR spectra.

[h] Overlapping with macrocycle absorption at 820 cm^{-1}.

TGA of the Dy complex showed a dehydration step at 50–85°C, corresponding to the loss of *ca* 1.5 H_2O, followed by a well-separated step at 95–120°C, corresponding to the loss of *ca* 2.5 H_2O.

The Er^{III}, Tm^{III}, Yb^{III} and Lu^{III} species gave yellow solutions from which a mixture of feathery yellow needles and ill-formed white crystals formed upon evaporation to near dryness. The two products have similar solubilities and could not be completely separated. The IR spectra of the mixtures were identical with those of the yellow Sm–Ho species, except for the additional presence of carboxylate absorptions of variable intensity.

The yellow $ML(CrO_4)_{1.5}\cdot H_2O$ complexes (M = Sm–Gd), when exposed to the atmosphere in their mother liquor, slowly redissolved and new products, of empirical formula $ML(CrO_4)(Cr_2O_7)_{0.5}\cdot nH_2O$ ($n = 0.5$–1.0), separated after 1–2 days as well-formed crystals in 20–30% yields. The products were gold-coloured when obtained and stored in the dark, red–brown when exposed to light. The red–brown crystals became opaque when stored over Drierite. Identical golden or red–brown products precipitated immediately, as microcrystalline powders, when aqueous solutions of the {ML} diacetate-chloride complexes were treated with a mixture of potassium chromate and potassium dichromate ($\{ML\}^{3+}: CrO_4^{2-}: Cr_2O_7^{2-} = 1:1:0.5$). Yields *ca* 50%.

Dichromate complexes. Addition of $K_2Cr_2O_7$ to the {ML} diacetate-chlorides (M = La, Eu and Gd), in the same mole ratio and manner described above for K_2CrO_4, gave immediate brown microcrystalline precipitates of empirical formula $ML(Cr_2O_7)_{1.5}\cdot nH_2O$, ($n = 1.5$ for La, 2 for Eu and Gd). These products were insoluble in water and darkened when exposed to common organic solvents.

X-ray measurements and structure determination

Crystal data, collected reflections and parameters of the final refinement for $[CrO_4)LEu(\mu CrO_4)EuL(CrO_4)]\cdot 10H_2O$ and for $[ML(CrO_4)(H_2O)]_2\cdot(Cr_2O_7)\cdot 2H_2O$ with M = Sm, Eu are reported in Table 2. Reflections were collected using an Enraf–Nonius CAD-4 diffractometer for the Eu monomer, and a Philips PW1100 diffractometer for the Sm monomer and Eu dimer, using graphite-monochromated Mo-K_α radiation. The orientation matrix and cell dimensions were determined by least squares refinement of the angular positions of 25 reflections. Data were collected at room temperature. Three standard reflections were monitored every 2 h; linear isotropic decay (17.6%) was observed during data collection for the Eu monomer; the Sm monomer and Eu dimer did not show any significant decay. The intensities of the Eu monomer were corrected for decay; all intensities were corrected for Lorentz polarization and absorption.[7] Scattering factors and anomalous scattering corrections were taken from ref. 8.

The positions of the heavy atoms (Ln and Cr) were found from Patterson syntheses. All non-H atoms were located in the subsequent Fourier maps. The best refinements for the Sm and Eu monomers were achieved by placing a disordered dichromate ion around a symmetry centre in the space group $P\bar{1}$, with pp.* = 0.5 for the oxygen atoms bound to Cr(2). For the Eu dimer, the best refinement was achieved with a disordered bridging chromate around a symmetry centre in the space group $P\bar{1}$, with pp. = 0.5 for Cr(2), O(6) and O(7). (Refinement in the space group $P1$ did not give significant improvement in the structures.) The structures were refined by full-matrix least squares using anisotropic temperature factors for all non-hydrogen atoms except the oxygen atoms of the disordered $(Cr_2O_7)^{2-}$ and of the bridging CrO_4^{2-}. Final difference Fourier maps showed the positions of the hydrogen atoms; however, these were introduced at calculated positions in their described geometries (d_{C-H} 0.98 Å) and during refinement were allowed

Table 2. Experimental data for the crystallographic analyses

Compound	$EuL(CrO_4)(Cr_2O_7)_{0.5}\cdot 2H_2O$	$SmL(CrO_4)(Cr_2O_7)_{0.5}\cdot 2H_2O$	$Eu_2L_2(CrO_4)_3\cdot 10H_2O$
Formula	$EuCr_2O_{9.5}N_6C_{22}H_{30}$	$SmCr_2O_{9.5}N_6C_{22}H_{30}$	$Eu_2Cr_3N_{12}O_{22}C_{44}H_{72}$
Mol. wt	786.47	784.91	1581.03
Crystal size (mm)	0.19 × 0.24 × 0.26	0.22 × 0.31 × 0.18	0.20 × 0.28 × 0.16
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.468(2)	8.486(2)	11.103(3)
b (Å)	10.406(3)	10.334(2)	11.447(3)
c (Å)	15.809(2)	15.798(3)	12.568(3)
α (°)	98.82(2)	98.85(2)	98.29(4)
β (°)	93.55(2)	93.64(2)	110.47(3)
γ (°)	97.21(2)	97.40(2)	83.10(3)
V (Å^3)	1361.0(6)	1352.6(5)	1476.6(5)
Z	2	2	1 (dimer)
D_c (g cm^{-3})	1.92	1.93	1.78
$F(000)$	782	780	794
2θ range (°)	2–27	2–25	2–26
Radiation (λ, Å)	Mo-K_α(0.71069)	Mo-K_α(0.71069)	Mo-K_α(0.71069)
μ (cm^{-1})	31.08	28.37	25.58
T (K)	293	293	293
No. reflections collected	5323	6018	6073
No. observed $[I \geqslant 3\sigma(I)]$	4467	3844	5153
Weighting scheme w	$4F_o^2/[\sigma 2(F_o^2)+(0.04F_o^2)^2]$	$[\sigma^2(F_o)+0.004784(F_o)^2]^{-1}$	$[\sigma^2(F_o)+0.001812(F_o)^2]^{-1}$
$R = \Sigma[\lvert F_c\rvert - \lvert F_o\rvert]/\Sigma\lvert F_o\rvert$	0.043	0.062	0.035
$R_w = \Sigma w[\lvert F_o\rvert - \lvert F_c\rvert]^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.054	0.068	0.038
Goodness of fit	1.86	1.14	1.11

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* pp. = population parameter.

Table 3. Selected bond distances (Å) and angles (°) for EuL $(CrO_4)(Cr_2O_7)_{0.5}\cdot 2H_2O$

Eu—N(1)	2.640(4)	Eu—N(2)	2.670(5)
Eu—N(3)	2.576(5)	Eu—N(4)	2.656(5)
Eu—N(5)	2.671(5)	Eu—N(6)	2.563(5)
Eu—O(1)	2.369(4)	Eu—O(2)	2.386(4)
Eu—Ow(1)	2.391(5)	Cr(1)—O(1)	1.679(4)
Cr(1)—O(2)	1.665(4)	Cr(1)—O(3)	1.1633(5)
Cr(1)—O(4)	1.604(5)	Cr(2)—O(5)	1.585(12)
Cr(2)—O(6)	1.693(18)	Cr(2)—O(7)	1.701(23)
Cr(2)—O(8)	1.891(18)		
N—C(py)$_{av.}$	1.35(1)	C—C(py)$_{av.}$	1.38(1)
C—C(aliphatic)$_{av.}$	1.508(9)		
N(1)—Eu—N(2)	60.0(2)	N(1)—Eu—N(6)	61.3(2)
N(2)—Eu—N(3)	62.9(2)	N(3)—Eu—N(4)	60.6(2)
N(4)—Eu—N(5)	59.9(2)	N(5)—Eu—N(6)	62.7(2)
O(1)—Eu—O(2)	65.5(1)	O(1)—Eu—Ow(1)	148.8(2)
O(2)—Eu—Ow(1)	144.6(2)	O(1)—Cr(1)—O(2)	100.4(2)
O(1)—Cr(1)—O(3)	111.1(3)	O(1)—Cr(1)—O(4)	110.8(3)
O(2)—Cr(1)—O(3)	110.5(2)	O(2)—Cr(1)—O(4)	112.5(3)
O(3)—Cr(1)—O(4)	111.0(3)	O(5)—Cr(2)—O(6)	98.8(7)
O(5)—Cr(2)—O(7)	101.9(9)	O(5)—Cr(2)—O(8)	111.9(7)
O(6)—Cr(2)—O(7)	112.8(9)	O(6)—Cr(2)—O(8)	104.5(8)
O(7)—Cr(2)—O(8)	124.1(9)		

to ride on the attached carbon atoms with unique isotropic thermal parameters. The calculations were performed with the CAD4-SDP system of programs[9] for the Eu monomer, and with SHELX-76[10] for the Sm monomer and the Eu dimer. Selected bond distances and angles for the complexes are reported in Tables 3–5, torsion angles are in Tables 6–8.

Table 4. Selected bond distances (Å) and angles (°) for SmL(CrO_4) $(Cr_2O_7)_{0.5}\cdot 2H_2O$

Sm(1)—Cr(1)	3.082(2)	Sm(1)—O(1)	2.387(6)
Sm(1)—O(2)	2.405(7)	Sm(1)—Ow(1)	2.427(8)
Sm(1)—N(1)	2.633(7)	Sm(1)—N(2)	2.661(8)
Sm(1)—N(3)	2.593(9)	Sm(1)—N(4)	2.651(8)
Sm(1)—N(5)	2.676(8)	Sm(1)—N(6)	2.572(9)
Cr(1)—O(1)	1.662(7)	Cr(1)—O(2)	1.659(6)
Cr(1)—O(3)	1.617(8)	Cr(1)—O(4)	1.61(1)
Cr(2)—O(5)	1.58(1)	Cr(2)—O(7)	1.64(2)
Cr(2)—O(8)	1.76(3)		
N—C(py)$_{av.}$	1.35(1)	C—C(py)$_{av.}$	1.37(1)
C—C(aliphatic)$_{av.}$	1.50(1)		
N(5)—Sm(1)—N(6)	62.5(3)	N(4)—Sm(1)—N(5)	60.4(2)
N(3)—Sm(1)—N(4)	60.7(3)	N(2)—Sm(1)—N(3)	62.6(3)
N(1)—Sm(1)—N(6)	61.1(3)	N(1)—Sm(1)—N(2)	60.3(3)
O(2)—Sm(1)—Ow(1)	144.0(3)	O(1)—Sm(1)—Ow(1)	149.8(3)
O(1)—Sm(1)—O(2)	64.6(2)	O(3)—Cr(1)—O(4)	110.2(5)
O(2)—Cr(1)—O(4)	112.3(4)	O(2)—Cr(1)—O(3)	111.2(4)
O(1)—Cr(1)—O(4)	110.9(4)	O(1)—Cr(1)—O(3)	111.1(4)
O(1)—Cr(1)—O(2)	101.0(4)	O(7)—Cr(2)—O(8)	130(1)
O(5)—Cr(2)—O(8)	109(1)	O(5)—Cr(2)—O(7)	110.7(8)

Table 5. Selected bond distances (Å) and angles (°) for $Eu_2L_2(CrO_4)_3 \cdot 10H_2O$

Eu—N(1)	2.657(4)	Eu—N(2)	2.596(4)
Eu—N(3)	2.628(5)	Eu—N(4)	2.616(3)
Eu—N(5)	2.557(4)	Eu—N(6)	2.654(5)
Eu—O(1)	2.450(3)	Eu—O(2)	2.392(3)
Eu—O(5)	2.300(4)	Cr(1)—O(1)	1.676(4)
Cr(1)—O(2)	1.662(3)	Cr(1)—O(3)	1.615(4)
Cr(1)—O(4)	1.619(6)	Cr(2)—O(5)	1.696(5)
Cr(2)—O(5)′	1.796(4)	Cr(2)—O(6)	1.647(9)
Cr(2)—O(7)	1.635(9)		
N—C(py)$_{\text{av.}}$	1.338(7)	C—C(py)$_{\text{av.}}$	1.385(9)
C—C(aliphatic)$_{\text{av.}}$	1.507(9)		
N(5)—Eu—N(6)	63.3(1)	N(4)—Eu—N(5)	61.5(1)
N(3)—Eu—N(4)	61.1(1)	N(2)—Eu—N(3)	62.9(1)
N(1)—Eu—N(6)	60.2(1)	N(1)—Eu—N(2)	60.6(1)
O(2)—Eu—O(5)	147.2(1)	O(1)—Eu—O(2)	64.3(1)
O(3)—Cr(1)—O(4)	110.9(3)	O(2)—Cr(1)—O(4)	111.6(3)
O(2)—Cr(1)—O(3)	111.5(2)	O(1)—Cr(1)—O(4)	111.1(2)
O(1)—Cr(1)—O(3)	110.3(2)	O(1)—Cr(1)—O(2)	101.1(2)
O(6)—Cr(2)—O(7)	105.0(5)	O(5)—Cr(2)—O(7)	110.5(3)
O(5)—Cr(2)—O(6)	113.8(4)	O(5)—Cr(2)—O(5)′	102.9(2)

′, at $1-x$, $-y$, $1-z$.

Table 6. Selected bond distances (Å), angles (°) and torsion angles (°) for the L macrocycle of $EuL(CrO_4)(Cr_2O_7)_{0.5} \cdot 2H_2O$

Atoms	Distance 2—3 (Å)	Angles 1—2—3 (°)	Torsion angles 1—2—3—4 (°)
C(1)—N(1)—C(5)—C(6)	1.341(8)	117.8(5)	−177.5(5)
N(1)—C(5)—C(6)—N(2)	1.497(9)	116.0(5)	2.5(8)
C(5)—C(6)—N(2)—C(8)	1.260(7)	116.8(6)	176.3(5)
C(6)—N(2)—C(8)—C(9)	1.482(8)	118.2(5)	−163.2(6)
N(2)—C(8)—C(9)—N(3)	1.512(8)	108.2(5)	−54.6(6)
C(8)—C(9)—N(3)—C(10)	1.466(8)	107.5(5)	−92.3(7)
C(9)—N(3)—C(10)—C(12)	1.280(8)	119.9(6)	177.6(6)
N(3)—C(10)—C(12)—N(4)	1.487(10)	116.4(6)	−6.8(9)
C(10)—C(12)—N(4)—C(16)	1.362(8)	115.2(6)	176.7(6)
C(12)—N(4)—C(16)—C(17)	1.339(8)	117.7(5)	−179.2(6)
N(4)—C(16)—C(17)—N(5)	1.514(9)	115.4(5)	−7.6(9)
C(16)—C(17)—N(5)—C(19)	1.267(8)	116.6(6)	178.3(6)
C(17)—N(5)—C(19)—C(20)	1.464(10)	117.2(6)	−157.8(6)
N(5)—C(19)—C(20)—N(6)	1.513(10)	108.8(6)	−51.7(7)
C(19)—C(20)—N(6)—C(21)	1.462(8)	108.3(6)	−98.1(7)
C(20)—N(6)—C(21)—C(1)	1.286(7)	120.6(6)	179.4(5)
N(6)—C(21)—C(1)—N(1)	1.500(9)	115.3(6)	−9.8(8)
C(21)—C(1)-N(1)—C(5)	1.340(8)	116.4(5)	178.4(5)

RESULTS AND DISCUSSION

Synthesis and general features of the complexes

Reaction of K_2CrO_4 with the $[ML(CH_3OO)_2]Cl \cdot nH_2O$ complexes in aqueous solution resulted in complete anion metathesis for all members of the lanthanide series, without disruption of the metal-macrocycle moieties. The type of product obtained, however, depended on the size of the metal ion.

Among the larger lanthanides, La^{III}, Pr^{III} and Nd^{III} gave water-insoluble pale yellow micro-

Table 7. Selected bond distances (Å), angles (°) and torsion angles (°) for the L macrocycle of $SmL(CrO_4)(Cr_2O_7)_{0.5} \cdot 2H_2O$

Atoms	Distance 2—3 (Å)	Angles 1—2—3 (°)	Torsion angles 1—2—3—4 (°)
C(1)—N(1)—C(5)—C(6)	1.35(1)	116.8(8)	−178.3(9)
N(1)—C(5)—C(6)—N(2)	1.47(2)	116.2(9)	4(1)
C(5)—C(6)—N(2)—C(8)	1.28(1)	117.7(9)	175.7(9)
C(6)—N(2)—C(8)—C(9)	1.48(1)	119.0(9)	−163.9(9)
N(2)—C(8)—C(9)—N(3)	1.50(1)	108.9(9)	−54(1)
C(8)—C(9)—N(3)—C(10)	1.46(1)	107.7(9)	−92(7)
C(9)—N(3)—C(10)—C(12)	1.29(1)	120.2(9)	177.3(9)
N(3)—C(10)—C(12)—N(4)	1.48(2)	116.3(9)	−8(9)
C(10)—C(12)—N(4)—C(16)	1.36(1)	115.6(9)	177.5(9)
C(12)—N(4)—C(16)—C(17)	1.34(1)	118.0(9)	−179.2(6)
N(4)—C(16)—C(17)—N(5)	1.48(2)	116.3(9)	−9(1)
C(16)—C(17)—N(5)—C(19)	1.29(1)	117.3(9)	179.6(9)
C(17)—N(5)—C(19)—C(20)	1.45(1)	118.9(9)	−157.6(9)
N(5)—C(19)—C(20)—N(6)	1.51(2)	108.8(9)	−53(1)
C(19)—C(20)—N(6)—C(21)	1.44(1)	108.5(9)	−97(1)
C(20)—N(6)—C(21)—C(1)	1.29(1)	121.6(9)	179.7(9)
N(6)—C(21)—C(1)—N(1)	1.51(1)	116.4(9)	−10(1)
C(21)—C(1)-N(1)—C(5)	1.34(1)	114.6(8)	177.3(9)

Table 8. Selected bond distances (Å), angles (°) and torsion angles (°) for the L macrocycle of $Eu_2L_2(CrO_4)_3 \cdot 10H_2O$

Atoms	Distance 2—3 (Å)	Angles 1—2—3 (°)	Torsion angles 1—2—3—4 (°)
C(1)—N(1)—C(5)—C(7)	1.339(7)	118.3(4)	−177.1(4)
N(1)—C(5)—C(7)—N(2)	1.511(7)	115.8(5)	2.5(7)
C(5)—C(7)—N(2)—C(8)	1.269(7)	115.9(5)	−177.2(4)
C(7)—N(2)—C(8)—C(9)	1.452(7)	122.6(5)	103.9(6)
N(2)—C(8)—C(9)—N(3)	1.507(8)	108.1(5)	52.5(6)
C(8)—C(9)—N(3)—C(10)	1.459(6)	109.3(5)	164.1(5)
C(9)—N(3)—C(10)—C(12)	1.271(6)	118.8(5)	−174.6(4)
N(3)—C(10)—C(12)—N(4)	1.497(7)	117.3(5)	4.8(7)
C(10)—C(12)—N(4)—C(16)	1.336(7)	115.9(4)	175.7(4)
C(12)—N(4)—C(16)—C(17)	1.343(6)	118.8(4)	−179.2(4)
N(4)—C(16)—C(17)—N(5)	1.490(8)	116.2(4)	1.5(7)
C(16)—C(17)—N(5)—C(19)	1.281(6)	116.1(5)	−176.6(4)
C(17)—N(5)—C(19)—C(20)	1.473(8)	122.1(5)	100.7(6)
N(5)—C(19)—C(20)—N(6)	1.495(8)	108.1(5)	53.6(6)
C(19)—C(20)—N(6)—C(21)	1.480(8)	108.7(5)	169.2(5)
C(20)—N(6)—C(21)—C(1)	1.258(7)	119.1(5)	−173.2(5)
N(6)—C(21)—C(1)—N(1)	1.499(8)	117.4(5)	−4.9(7)
C(21)—C(1)—N(1)—C(5)	1.336(7)	115.8(5)	175.0(4)

crystals of stoichiometry $ML(CrO_4)_{1.5} \cdot 5.5H_2O$; Ce^{III} was oxidized to Ce^{IV} and gave a golden-brown product, also insoluble in water, with stoichiometry $Ce(CrO_4)_2 \cdot 6H_2O$. The four complexes of this group had identical IR spectra which showed, in addition to the absorptions characteristic of water[11] and of the macrocyclic ligand,[12] an extremely intense and fairly sharp absorption at *ca* 897 cm^{-1} [Fig. 2(a)], arising from the antisymmetric Cr—O stretching mode (ν_3) of ionic CrO_4^{2-}.[13] When heated in the solid state above 110°C in a dry and inert atmosphere, these complexes lost water quantitatively,

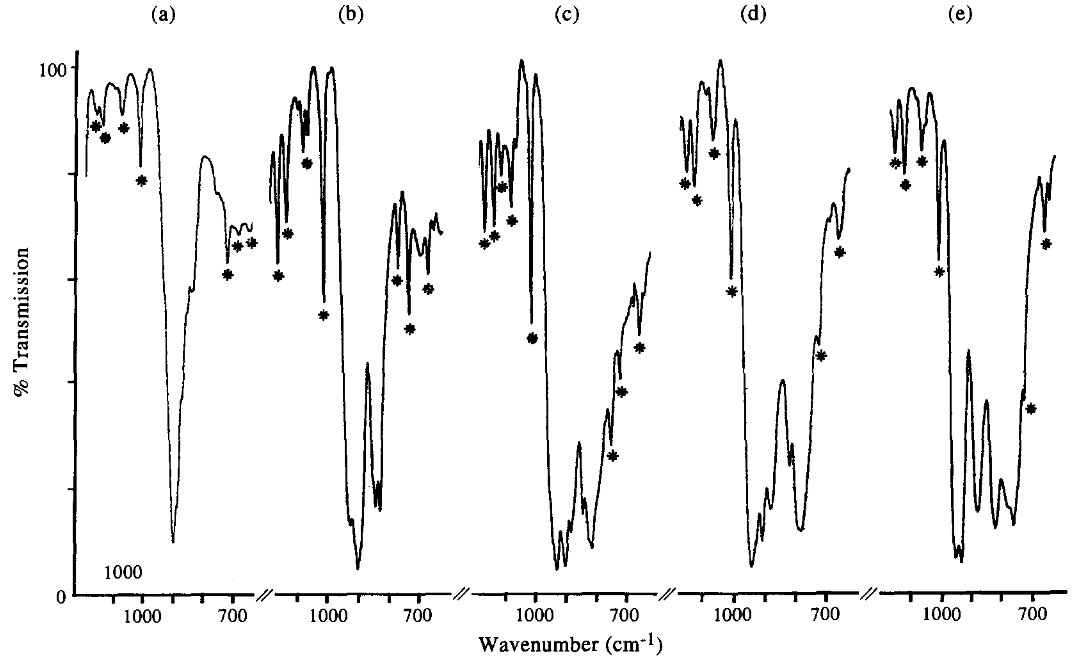

Fig. 2. IR spectra

but rehydrated rapidly upon exposure to moisture. In the IR spectra of the anhydrous species, the absorption arising from the $\nu_3(CrO_4)$ mode was broader than in the hydrated analogues and showed partly resolved maxima at 897 and 818 cm^{-1}, suggesting at least partial coordination of the chromate anion.

With the lanthanides of intermediate size, Sm^{III}–Ho^{III}, a series of bright yellow products, of stoichiometry $ML(CrO_4)_{1.5} \cdot nH_2O$ with $n = 4$ or 5, were first obtained from the metathesis reaction. The IR spectra of these compounds were nearly identical to one another and contained, in addition to the absorptions of water and of the organic ligand, two intense and fairly well resolved absorptions in the Cr—O stretching region. These absorptions, centred at *ca* 900 and 820 cm^{-1}, showed appreciable splitting [Fig. 2(b)], suggesting the presence of non-equivalent CrO_4^{2-} species of approximate C_{2v} symmetry.[13] This spectral pattern is consistent with the dinuclear coordination formula $[(CrO_4)LM(\mu\text{-}CrO_4)ML(CrO_4)] \cdot 10H_2O$, established by X-ray analysis (see later). The yellow complexes were indefinitely stable when dry, but gradually changed to compounds of stoichiometry $ML(CrO_4)(Cr_2O_7)_{0.5} \cdot nH_2O$ ($n = 1$ or 2) when exposed to the atmosphere in the presence of their mother liquor. The new products were light sensitive; in the dark they were obtained as gold-coloured crystals but changed irreversibly to red–brown upon exposure to light. The IR spectra of the red–brown species showed the usual macrocycle pattern, a medium-intensity absorption in the O—H stretching region, and very intense, multiple, and only partly resolved peaks in the Cr—O stretching region [Fig. 2(c)]. These absorptions are consistent with the coordination formula $[ML(CrO_4)(H_2O)]_2(Cr_2O_7) \cdot 2H_2O$, established by X-ray analysis (see later) and containing both chelating chromate[13] and ionic dichromate.[14]

In an attempt to analyse the Cr—O stretching region in the IR spectra of the red–brown species, dichromate-only complexes were prepared with $\{LaL\}^{3+}$, $\{EuL\}^{3+}$ and $\{GdL\}^{3+}$. The resulting products had nearly identical stoichiometries, corresponding to $ML(Cr_2O_7)_{1.5} \cdot nH_2O$, with $n = 1.5$ for La and 2 for Eu or Gd. Their IR spectra, however, were quite different. The spectrum of the La^{III} complex [Fig. 2(d)] showed the dichromate to be ionic only;[14] whereas the spectra of the {EuL} and {GdL} complexes, identical to one another, showed a different set of intense bands in the Cr—O stretching region [Fig. 2(e)] suggesting the presence of coordinated dichromate. X-ray quality crystals of these {EuL} and {GdL} dichromates could not be obtained and their structures remain undetermined.

With the smaller members of the lanthanide series, Er^{III}–Lu^{III}, no pure products could be obtained by acetate-chromate metathesis, as the solubility of the {ML}-chromate species increased dramatically with decreasing metal size.

Crystal structures of the yellow complex of stoichiometry $EuL(CrO_4)_{1.5} \cdot 5H_2O$ *and of the red–brown complexes of stoichiometry* $ML(CrO_4)(Cr_2O_7)_{0.5} \cdot 2H_2O$ *with* $M = Sm^{III}$ *and* Eu^{III}

X-ray analysis of the bright yellow Eu^{III} complex showed that this compound has the coordination formula $[(CrO_4)LM(\mu\text{-}CrO_4)ML(CrO_4)] \cdot 10H_2O$. The centrosymmetric dinuclear molecule consists of two $\{EuL\}^{3+}$ moieties joined through a bridging chromate group, which is linked to each Eu^{III} *via* a single oxygen atom. The $\{EuL\}^{3+}$ moieties have a somewhat folded configuration, with the concave sides of the macrocycles facing each other across the bridging chromate. A bidentate chelating chromate on the convex side completes the coordination sphere of each Eu^{III}. The bridging chromate is present in two alternative positions (50% probability) close to a crystallographic inversion centre and is somewhat asymmetric, with the Cr—O bond lengths of the two coordinated oxygens differing from one another (Cr(2)—O(5) 1.696(5) Å; Cr(2)—O(5)′ 1.796(4) Å) and differing also from those of the uncoordinated oxygens (Cr(2)—O(6) 1.647(9) and Cr(2)—O(7) 1.635(9) Å, respectively).

An ORTEP[15] view of the dinuclear molecule is illustrated in Fig. 3; for clarity, only one of the positions occupied by the bridging chromate is shown in the diagram. It should be noted that a similar arrangement of the exocyclic ligands, with a single donor atom on the concave side of the macrocycle and two donor atoms on the less hindered convex side, has been observed in other 9-coordinate complexes of this macrocycle.[5] The ten water molecules present in the unit cell form a network of hydrogen bonds, either with one another or with the neighbouring oxygens of the chromate ligands, as illustrated in Fig. 4; the most significant oxygen—oxygen contacts are listed in Table 9.

Analysis of the red–brown Sm^{III} and Eu^{III} compounds showed that they are strictly isostructural and have the coordination formula $[ML(CrO_4)(H_2O)L]_2(Cr_2O_7) \cdot 2H_2O$. In the complex cation the metal centre is bound to the six-nitrogen-donor atoms of the macrocyclic ligand, which has the usual folded configuration. A bidentate chelating chromate on the convex side of the macrocycle and a water molecule on the opposite side complete the coordination sphere. Ionic dichromate (one for every two complex cations) provides the ionic charge balance. An ORTEP view of the complex cation is shown in Fig. 5. The crystal packing is determined by a three-dimensional network of hydrogen bonds, mainly occurring between the H atoms of the water molecules and the O atoms of the chromates and dichromates.

A comparison between the yellow and the red–brown Eu^{III} complexes reveals marked structural similarities. In both species the Eu^{III} is 9-coordinated and the $\{EuL\}^{3+}$ moieties have the folded 'butterfly' configuration common to other lanthanide complexes of this ligand.[3–5] In both species

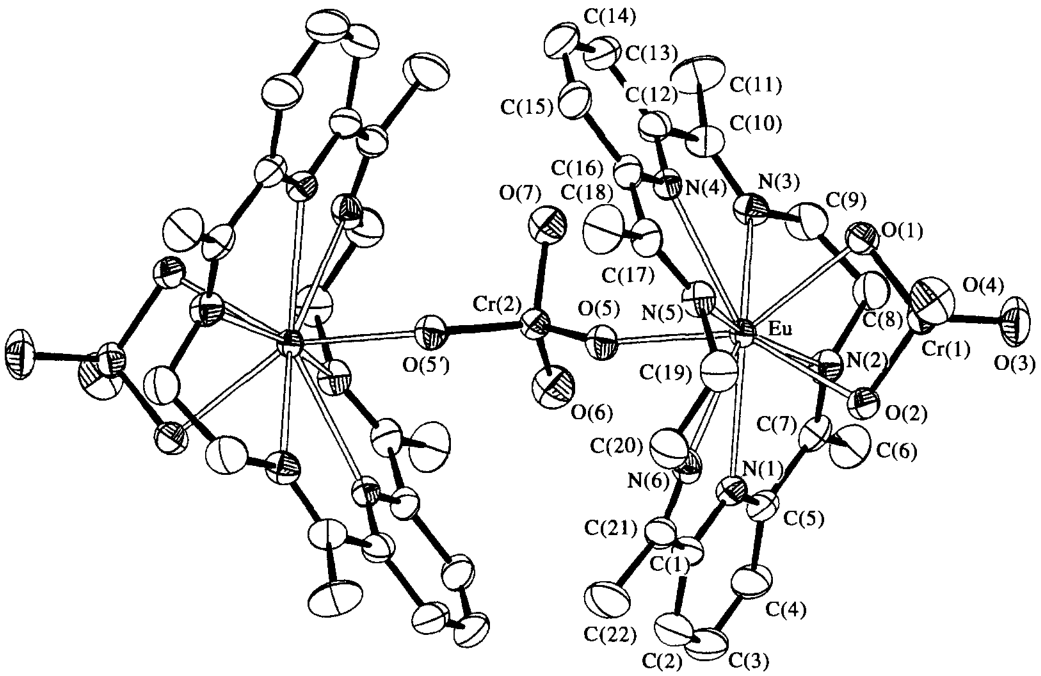

Fig. 3. ORTEP view of dinuclear $[(CrO_4)LEu(\mu\text{-}CrO_4)EuL(CrO_4)]$ complex. For clarity, only one of the positions occupied by the bridging chromate is shown.

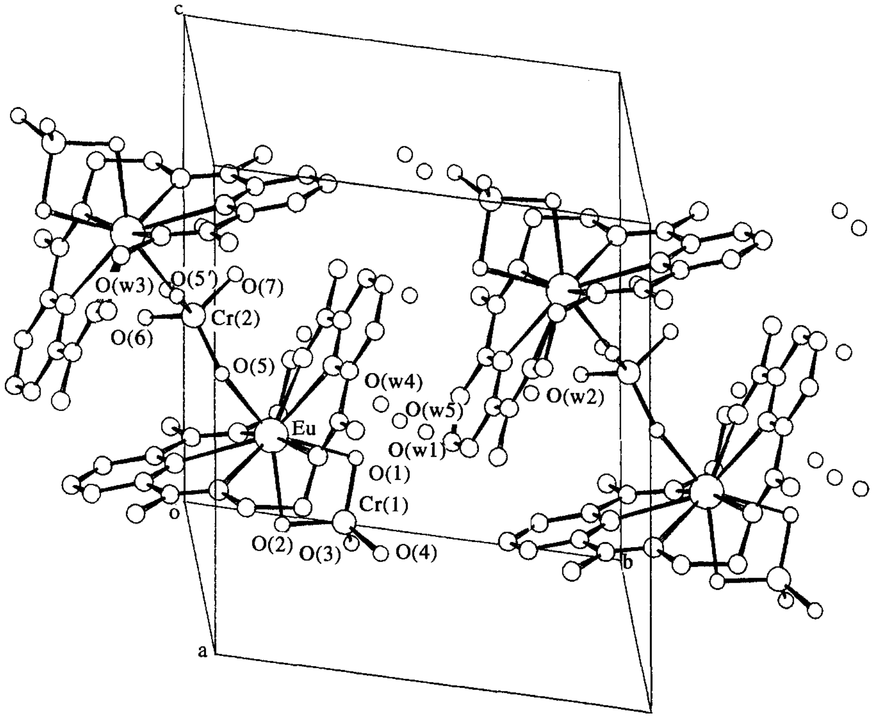

Fig. 4. Cell content of [(CrO4)LEu(μ-CrO_4)EuL(CrO_4)] · $10H_2O$ viewed down the *a* axis.

Table 9. Selected significant contact distances (less than 3 Å) involving the uncoordinated water molecules in [(CrO4)LEu(μ-CrO_4)EuL(CrO_4)] · $10H_2O$

Ow(1) ··· Ow(2)	2.919(7)	Ow(1) ··· Ow(4)	2.926(12)
Ow(4) ··· Ow(5)	2.440(12)	O(3) ··· Ow(1)^{i}	2.789(7)
O(4) ··· Ow(5)^{i}	2.599(14)	O(4) ··· Ow(5)^{ii}	2.791(12)
O(6) ··· Ow(2)^{iii}	2.810(11)	O(7) ··· Ow(3)^{iv}	2.944(12)
Ow(2) ··· Ow(3)^{v}	2.800(9)	Ow(3) ··· Ow(3)^{iv}	2.789(8)
Ow(5) ··· Ow(5)^{vi}	2.389(13)		

^{i}, $-x, 1-y, -z$; $^{ii}1+x, y, z$; $^{iii}x, 1-y, z$; ^{iv}, $-x, -y, 1-z$; ^{v}, $x, 1+y, z$; ^{vi}, $-1-x, 1-y, -z$.

the ligand as a whole has almost perfect non-crystallographic C_2 symmetry, relative to an axis very nearly perpendicular to the (average) plane of the six-nitrogen-donor atoms. The corresponding Eu—N distances are comparable in the two complexes (Tables 3 and 5) and the angles between the least-squares planes of the two macrocycle 'wings' hinged at the —CH_2—CH_2— side-chains have similar values (123.2(4)° for the yellow dimer and 124.9(2)°* for the red–brown monomer). The torsion angles of the two —CH_2—CH_2— side chains of the yellow dimer are fairly close to one another [N(2)—C(8)—C(9)—N(3) 52.5(6)° and N(5)—C(19)—C(20)—N(6) 53.6(6)°] and are comparable to the corresponding values in the red–brown monomers [N(2)—C(8)—C(9)—N(3) −54.6(6)° for Eu and −54(1)° for Sm; N(5)—C(19)—C(20)—N(6) −51.7(7)° for Eu and −53(1)° for Sm]. In both types of complexes the chromium atom and the average positions of the O(1), O(2), O(3) and O(4) atoms of the bidentate chelating chromate are situated almost exactly on the C_2 axis. The only significant differences between the yellow dimer and the red–brown Eu monomer involve the Eu—O distances. For the chelating chromate, the Eu—O bonds in the red–brown cationic monomer are shorter and more symmetric (2.369(4) and 2.386(4) Å) than in the yellow molecular

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* The corresponding value for the Sm analogue is 124.2(2)°.

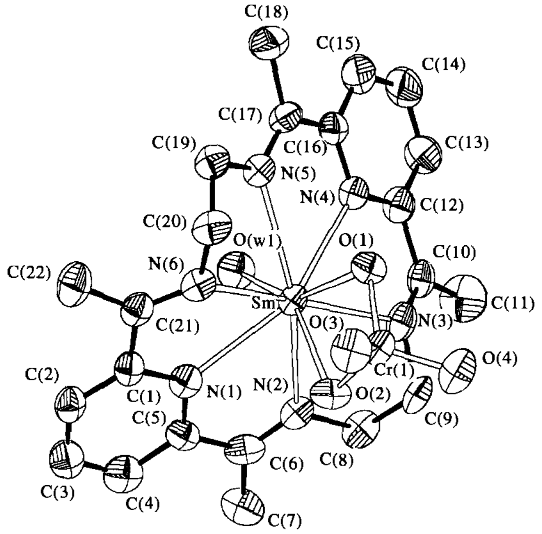

Fig. 5. Perspective ORTEP drawing of the $[SmL(CrO_4)(H_2O)]^+$ complex cation, with the atom numbering scheme.

dimer (2.450(3) and 2.392(3) Å); all these bonds are significantly longer than the Eu—O bonds of the bridging chromate (2.300(4) Å) in the dimer. These values are comparable to those reported for the bridging chromate of the dimeric $[Tb_2(CrO_4)_3(H_2O)_5] \cdot 2H_2O$, where the Cr—O bond lengths for the oxygens linked to Tb are 1.627(8) and 1.668(6) Å, whereas the Cr—O bond lengths for the terminal oxygens are 1.664(6) and 1.648(6) Å.

CONCLUSIONS

This work has shown that in complexes containing the $\{ML\}^{3+}$ lanthanide-macrocycles the chromate ion can play a variety of roles (simple counterion, chelating ligand, bridging group) which can occur singly or together. The choice of role appears to depend primarily on the size of the lanthanide ion, with the larger lanthanides favouring ionic chromate and the lanthanides of intermediate and smaller size preferring coordinated chromate. For the intermediate lanthanides, the pH-dependent chromate–dichromate equilibrium also becomes important, and the presence in solution of even minor concentrations of the dichromate ion may result in major changes in the composition and structure of the products. The crystal structures described here are significant, not only because they provide detailed information on two novel types of complexes, but also because they are the first structures reported for metal–chromate/dichromate complexes containing organic ligands. When considered in conjunction with the parallel spectral studies, these crystal structures support the reliability of IR spectra in the rapid identification of the bonding mode(s) of chromate and dichromate groups in metal complexes.

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