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SYNTHESIS, X-RAY CRYSTAL STRUCTURE AND SPECTROSCOPY OF THE HYDROGEN-BRIDGED DIMER [Cr^{III}($L \cdot H_3L$)Cr^{III}][PF_6]$_3$ (H_3L = *N*,*N*′,*N*″-TRIS[(2*S*)-2-HYDROXYPROPYL]-1,4,7-TRIAZACYCLONONANE)

LOUIS J. FARRUGIA, NORMAN M. MACDONALD,
ROBERT D. PEACOCK* and JOHN ROBB

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, U.K.

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Abstract—The preparation, structure and spectroscopy of [Cr^{III}($L \cdot H_3L$)Cr^{III}][PF_6]$_3$ (H_3L = *N*,*N*′,*N*″-tris[(2*S*)-2-hydroxypropyl]-1,4,7-triazacyclononane) are presented. The complex is a hydrogen-bridged dimer with three symmetric O—H—O bridges. The coordination round the Cr^{III} is preudo-octahedral with a twist away from octahedral geometry of 15°. The dimer is broken up under both acid and basic conditions to give [$Cr^{III}LH_3$]$^{3+}$ and [$Cr^{III}L$], respectively. The CD spectra of the three species are interpreted as showing that there is a smaller twist away from octahedral geometry in the monomers than in the dimer. The preparation of [Cr^{III}(*S*-mtcta)] (*S*-mtcta = *N*,*N*′,*N*″-trisacetato-(2*S*)-2-methyl-1,4,7-triazacyclononane) is also reported and its spectra compared with those of [Cr^{III}($L \cdot H_3L$)Cr^{III}]$^{3+}$.

There are very few structurally characterized Cr^{III} complexes of triaza macrocycles or their pendant arm derivatives.[1] The "parent" complex [$Cr(tacn)_2$]$^{3+}$ (tacn = 1,4,7-triazacyclononane) has not had its crystal structure determined (although the hydroxide-bridged trimer and dimer, [$Cr_3(tacn)_3(OH)_5I_5$]$\cdot 5H_2O$ and [$Cr_2(tacn)_2(OH)_2(CO_3)$]$I_2 \cdot H_2O$ respectively, have been crystallographically characterized[2,3]). [Cr^{III}(tcta)] (tcta = *N*,*N*′,*N*″-trisacetato-1,4,7-triazacyclononane) has had its structure determined,[4] as has [Cr^{III}($L' \cdot H_3L'$)Cr^{III}]$^{3+}$ (L′ = *N*,*N*′,*N*″-tris-[2-hydroxyethyl]-1,4,7-triazacyclononane), although in this case the structure was severely disordered.[5] Cr^{III} complexes of the amine pendant arm ligand *N*,*N*′,*N*″-tris-2-[aminoethyl]-tris-1,4,7-triazacyclononane[6] and the "bulky arm" ligand *N*,*N*′,*N*″-tris-[(2*R*)-2-hydroxy-3-methyl-butyl]-1,4,7-triazacyclononane[7] have been reported but no structures determined.

As part of our investigation[8–11] of the chemistry of the chiral-pendant-arm ligand *N*,*N*′,*N*″-tris[(2*S*)-2-hydroxypropyl]-1,4,7-triazacyclononane (H_3L), we report the preparation, structural characterization and spectroscopy of the Cr^{III} hydrogen-bridged dimer [Cr^{III}($L \cdot H_3L$)Cr^{III}][PF_6]$_3$. Additionally, we have prepared a chiral analogue of the tcta ligand, *N*,*N*′,*N*″-trisacetato-(2*S*)-2-methyl-1,4,7-triazacyclononane (*S*-mtcta), and report the spectroscopic properties of its Cr^{III} complex.

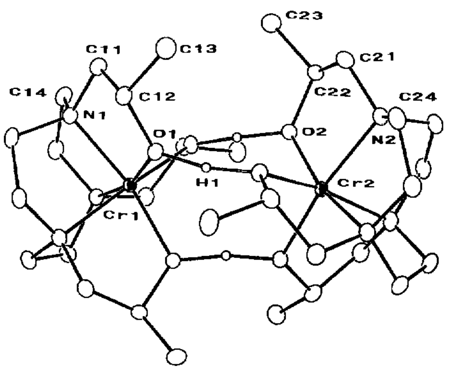

Fig. 1. View of the [$Cr(L \cdot H_3L)Cr$]$^{3+}$ cation.

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*Author to whom correspondence should be addressed.

EXPERIMENTAL

H_3L was prepared as described previously.[8] *S*-mtcta was synthesized by the method published[4] for the unmethylated analogue, tcta, substituting (2*S*)-2-methyl-1,4,7-triazacyclononane[12] for the unmethylated macrocycle.

Synthesis of $[Cr^{III}(L\cdot H_3L)Cr^{III}][PF_6]_3$

A solution containing 0.259 g (0.97 mmol) $CrCl_3\cdot 6H_2O$ in 30 cm^3 DMSO was heated to 175°C and this temperature maintained until the volume had been reduced by approximately 5 cm^3. The resulting solution, which contains dehydrated $CrCl_3$ as the DMSO solvate, was cooled to 70°C under dinitrogen and a solution containing 0.30 g (0.98 mmol) of LH_3 in dry ethanol added. The mixture was maintained at 70°C for 30 min and then cooled. The complex was purified by absorption on SP-Sephadex followed by elution with 0.1 mol dm^{-3} NaCl solution. The first two pink bands were discarded; the third, purple, band was collected and precipitated with ammonium hexafluorophosphate. The purple solid was recrystallized from acetonitrile. Yield 0.125 g (11% based on H_3L). Found: C, 31.3; H, 5.4; N, 7.5. Calc. for $C_{30}H_{63}Cr_2F_{18}N_6O_6P_3$: C, 31.5; H, 5.6; N, 7.4%.

Synthesis of [Cr(*S*-mtcta)]

To 1 cm^3 of a 0.5 mol dm^{-3} aqueous solution of *S*-mtcta (5×10^{-4} mol) was added 0.12 g (4.5×10^{-4} mol) of $CrCl_3\cdot 6H_2O$ in 1 cm^3 of water. On refluxing (2 h) the solution turned from its initial green colour, through purple, to deep red. The solution was concentrated to 0.5 cm^3 and left in the refrigerator until red needle-like crystals appeared. Yield 0.1 g (60%). Found: C, 42.3; H, 5.6; N, 11.3. Calc. for $C_{13}H_{20}CrN_3O_6$: C, 42.6; H, 5.5; N, 11.5%.

Crystal structure determination of $[Cr^{III}(L\cdot H_3L)Cr^{III}][PF_6]_3$

Details of the data collection procedures and structural refinements are given in Table 1. Data were collected on an Enraf–Nonius CAD4F automated diffractometer with graphite monochromated X-radiation ($\lambda = 0.71069$ Å). Unit cell parameters were determined by refinement of the setting angles of 25 reflections using the SET4 routine. DIFABS (max/min corrections 1.11 and 0.90) were applied.

The statistics of the normalized structure factors and systematic absences uniquely indicated the space group $P2_13$. The coordinates of the non-hydrogen atoms (apart from the disordered fluorine atoms in one PF_6 group) were taken from the isostructural cobalt complex,[8] $[Co^{III}(L\cdot H_3L)Co^{III}][PF_6]_3$. Refinement was by full matrix least squares, minimizing the function $\Sigma w(|F_0|-|F_c|)^2$ with the weighting scheme $w = [\sigma^2(F_0)]^{-1}$ used and judged satisfactory. $\sigma(F_0)$ was estimated from counting statistics. All non-hydrogen atoms were allowed anisotropic thermal motion. The aliphatic C—H hydrogen atoms were included at calculated positions (C—H = 1.0 Å), while the position of the O—H hydrogen H(1) was determined from a difference Fourier. All C—H atoms were allowed to ride on their attached carbon with one common refined isotropic thermal parameter. The positional and isotropic parameters of H(1) were freely refined. The e.s.d. of an observation of unit weight (S) was 2.71. The correctness of the enantiomer was confirmed by refinement of the η parameter,[13] which converged to a value of 0.98(5), with $(1+|\eta|)/\sigma(\eta) = 36.5$. Refinement using the inverted configuration converged with significantly higher residuals of R (R_w) 0.038 (0.036). Neutral atom scattering factors were taken from ref. 14 with corrections applied for anomalous scattering. All calculations were carried out on a microVAX 3600 computer using the Glasgow GX suite of programs.[15]

RESULTS AND DISCUSSION

Crystal structure of $[Cr^{III}(L\cdot H_3L)Cr^{III}][PF_6]_3$ (**1**)

The structure of the $[Cr^{III}(L\cdot H_3L)G^{III}]^{3+}$ cation is shown in Fig. 1. Important bond lengths and angles are collected in Table 2 and a comparison of selected geometric parameters with other relevant complexes made in Table 3. Compound **1** is isomorphous with the analogous Co^{III} complex[8] $[Co^{III}(L\cdot H_3L)Co^{III}][PF_6]_3$, having the same $\Delta(\lambda\delta)$ configuration. The main difference between the two complexes lies in the hydrogen bridges between the two halves of the dimer, which are symmetric in **1** and asymmetric in $[Co^{III}(L\cdot H_3L)Co^{III}][PF_6]_3$ (see Table 3). The geometries of the two halves of the dimer of **1** are essentially identical. The twist away from octahedral geometry (15°) is somewhat larger than in the Co^{III} dimer (10–11°)[8] or in the isoelectronic Mn^{IV} complex $[MnL]^-$ (11°)[10] and slightly smaller than the Ni^{II} species (17.5°).[9] Models suggest that the most stable dimer geometry is one in which one half is pseudo-octahedral and one trigonal prismatic, as is found[10,11] in $[Mn^{IV}(L\cdot H_3L)Mn^{II}]^{3+}$ and $[V^{IV}(L\cdot H_3L)Zn^{II}]^{3+}$. Thus, the 15° twist, which is large for a d^3 ion, is considered to be partly caused by the locking of the

Table 1. Experimental data for the crystallographic study of **1**

Molecular formula	$C_{30}H_{63}Cr_2F_{18}N_6O_6P_3$
M	1142.76
Crystal system	cubic
Space group	$P2_13$ (no. 198, T^4)
a (Å)	16.406(3)
U (Å^3)	4416(2)
Z	4
D_c (g cm^{-3})	1.72
$F(000)$	2352
μ(Mo-K_α) (cm^{-1})	7.10
T (K)	298
Crystal size/mm	0.7 × 0.5 × 0.2
Scan mode	Θ–2Θ
2Θ range (°)	$2 < \Theta < 25$
Standards	−5 0 8, 8 4 3
Measured every (h)	2
Decay factor	none
Total no. of reflections	8691
No. independent	2600
No. used in refinement	2232
Observability criterion, n in $I > n\sigma(I)$	3.0
No. of refined parameters	183
R^a	0.029
R'^a	0.035
Largest remaining feature in electron density map (e Å^{-3})	+0.45 (max), −0.34 (min)
Mean/max Δ/σ	0.003/0.053

[a] $R = \Sigma |F_0| - |F_c|/\Sigma|F_0|$, $R' = [\Sigma w(|F_0| - |F_c|)^2/\Sigma |F_0|/\Sigma w F_0^2]^{1/2}$.

Table 2. Selected bond lengths (Å) and bond angles (°) for **1**

Cr(1)—N(1)	2.071(3)	Cr(1)—O(1)	1.971(2)
Cr(2)—N(2)	2.070(3)	Cr(2)—O(2)	1.969(2)
O(1)—H(1)	1.22(5)	O(2)—H(1)	1.25(5)
N(1)—Cr(1)—N(1)	84.2(1)	O(1)—Cr(1)—O(1)	95.5(1)
N(2)—Cr(2)—N(2)	84.1(1)	O(2)—Cr(2)—O(2)	95.3(1)
O(1)—H(1)—O(2)	168.2(37)		

Table 3. Bond lengths (Å) and twist away from octahedral geometry, ϕ (°), for $[Cr^{III}(L \cdot H_3L)Cr^{III}]^{3+}$ and related complexes

	M—N (Å)	M—O (Å)	O—H (Å)	ϕ (°)	Ref.
$[Cr(L \cdot H_3L)Cr]^{3+}$	2.071[a]	1.970[a]	1.235[a]	15[a]	this work
$[Mn^{IV}L]$	2.051	1.857	1.841	11	10
[CoL]	1.944	1.939	1.62	11	8
$[Co(LH_3)]^{3+}$	1.954	1.939	0.90	10	8
[Cr(tcta)]	2.056	1.956		11	4

[a] Average values.

two halves into the dimer structure and is expected to be somewhat less in the corresponding protonated or deprotonated monomers. This suggestion is supported by the CD spectra of the dimer and monomers (see below).

Absorption and CD spectra of **1**

The absorption and CD spectra of **1** in MeCN solution (dimer) are shown in Fig. 2b and the spectra obtained after the addition of two drops of trifluoroacetic acid (protonated monomer) and two drops of triethylamine (deprotonated monomer) in Fig. 2a and c, respectively. Figure 3 shows the absorption and CD spectra of the analogous complex [Cr(S-mtcta)] for comparison. The absorption spectra of **1** behave in a similar, but more pronounced manner, to those of the Co^{III} dimer, moving to shorter wavelengths as the degree of protonation of the oxygen ligators increases. Thus, Δ_0 (cm^{-1}) is 17,360 for the monomer with alkoxide ligators, 18,380 for the hydrogen-bridged dimer and 19,380 for the fully protonated (alcohol ligators) monomer. This can be ascribed to the increased participation of $p\pi$–$d\pi$ bonding as the ligator changes from O—H (one available $p\pi$ orbital) to O— (two available $p\pi$ orbitals). This $p\pi$ participation is also reflected in the difference between the M—N and M—O bond lengths, which increase from 10.0 pm (**1**) or 8 pm ([Mn^{II}LH$_3$]$^{2+}$; alcohol ligators) to 20 pm ([Mn^{IV}L]$^+$; alkoxide ligators).

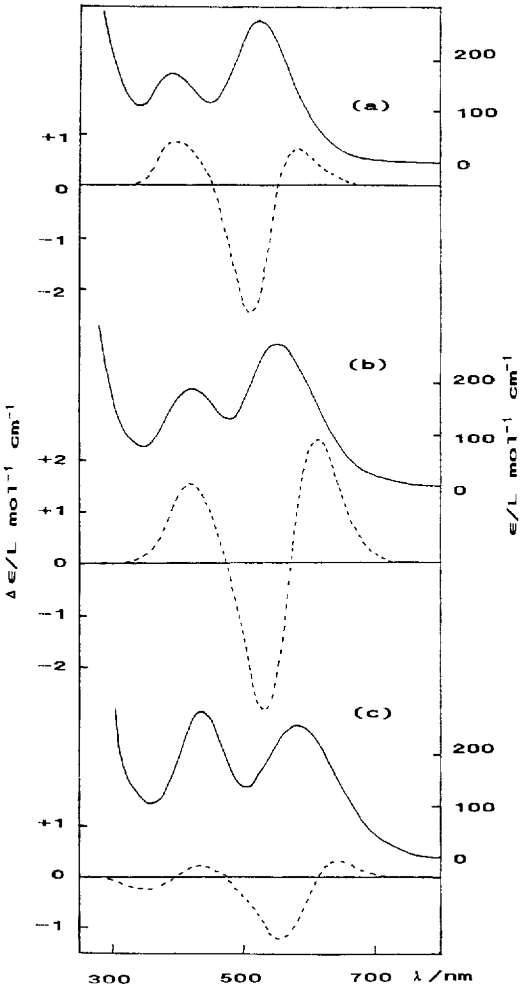

Fig. 2. Absorption (full line) and CD (dashed line) spectra of **1** in MeCN solution (b), and with the addition of two drops of F$_3$CCOOH (a) or Et$_3$N (c).

The CD spectra of **1** and its associated monomers are particularly interesting in that the magnitude of the CD is largest for the dimer and decreases on both protonation and deprotonation. The magnitude of a transition metal CD spectrum is dependent on a number of factors,[16] but in the present case most of these are invariant between the three species. It is tempting to suggest that the magnitude of the spectra reflects the degree of twist of the chiral chromophores and that the decrease of intensity on going from dimer to monomer is caused by the twist angle relaxing from the rather large 15° found in the dimer to something like the 10° twist found in the other d^3 species which have been structurally characterized.

The CD spectra of **1** and its associated monomers have the same sign pattern as the analogous Co^{III} species. Applying the same arguments leads to the lowest energy trigonal component of the $^4T_{2g}$ state being assigned A symmetry. This is the same as was found for [Cr(pd)$_3$][17] and [Cr(ox)$_3$]$^{3-}$,[18] but opposite to the situation in [Cr(en)$_3$]$^{3+}$,[19] where the E symmetry component is of lower energy.

Absorption and CD spectra of [Cr(S-mtcta)]

The absorption and CD spectra of [Cr(S-mtcta)] are shown in Fig. 3. While the structure of this complex has not been determined, that of the Cr^{III} complex with the unmethylated tcta ligand has[4] and shows the complex to have an 11° trigonal twist. The spectrum is of the enantiomer prepared from S-mtcta. Since R-mtacn is known to give endocyclic chelate rings with the λ conformation (in [Co(R-mtacn)$_2$]$^{3+}$),[20] S-mtcta will have endocyclic chelate rings with the δ conformation and so the absolute configuration of the complex is expected to be $\Lambda(\delta\lambda)$ and the twist to be anticlockwise. This is consistent with the sign of the CD spectrum. It is interesting to note that the spectra (both absorption and CD) of [Cr(S-mtcta)] most closely resemble those of the protonated monomer [Cr(H$_3$L)]$^{3+}$. This is further evidence that the twist in the monomer is less than in the hydrogen-bridged dimer.

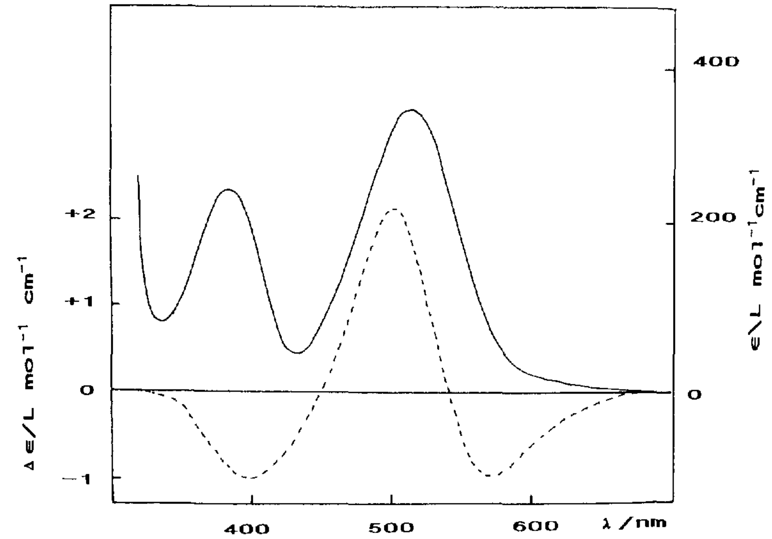

Fig. 3. Absorption (full line) and CD (dashed line) spectra of an aqueous solution of [Cr(*S*-mtcta)].

Electrochemistry of 1

The CV of **1** in dry DMSO at a gold electrode with 0.1 mol dm^{-3} TBAPF$_6$ as electrolyte shows a single quasi-reversible reduction at 1.14 V (vs NHE), with a small return oxidation wave at −0.99 V. This can be compared with [Cr(tcta)], where a reversible reduction was observed[4] at 1.41 V. The implication is that **1** is slightly more easily reduced than is [Cr(tcta)], but that the resulting Cr^{II} species is less chemically stable.

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