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Two dinuclear chromium(III) complexes and one mononuclear chromium(III) complex have been synthesized by the reaction of CrCl₃·6H₂O or trans-[Cr(py)Cl₂] (in 2-methoxyethanol) with tetrahydrosalen and substituted tetrahydrosalen derivatives L¹, L² and L³ (in the following L denotes the anions of H₂L¹, H₂L² or HL²). H₂L¹ = N,N'-bis(2-hydroxybenzyl)-1,2-ethanediame and HCl₃ = N,N'-bis(2-hydroxybenzyl)-trans-(S,S)-1,2-cyclohexanediamine and HL² = N-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-N'-(1-(2-pyridyl)ethyl)-1,1-dimethyl-1,2-ethanediame. Two new complexes with the stoichiometric formulae [CrLCl₁] (L = L¹ and L²) and one new complex with the stoichiometric formula [CrLCl₂] (L = L³) were obtained.

The crystal structure of [CrLCl₁]₂ has been determined. The crystal system is orthorhombic, the lattice constants are a = 8.205(1), b = 15.631(2), c = 24.426(1) Å, the volume of the unit cell is 3132.95(36) Å³. The space group is Pbcn. The refinement of 207 variables includes 2146 of the 3264 independent reflections. The final residual is 3.94%. The dinuclear molecule consists of two slightly distorted octahedrally cis-coordinated chromium centres bound together by two pheno xo bridges. The Cr–O–Cr angle is 100.84(9)° and the Cr–O(bridge) distances are 2.023(2) and 2.024(2) Å, respectively. The configuration of the dinuclear molecule is Δ, where A and A refer to the configuration of the two N,O chelates of the salen ligand. The Cr(1)–Cr(1)* distance is 3.118 Å.

The two complexes [CrLCl₁]₂ and [CrLCl₂]₂ behave as typical antiferromagnetically coupled dinuclear compounds with J-values of 17.1 and 16.7(1) cm⁻¹, respectively. The EPR spectrum of [CrLCl₁]₂ in a frozen glass (N-methylformamide) was measured at 80 K and is a typical spectrum from the quintet state which emerges as a result of the antiferromagnetic coupling of the two chromium(III) ions in the dinuclear complex. The spectrum was simulated using the parameters g = 1.98, J = 16.7 cm⁻¹, D₂ = 0.061 cm⁻¹ and E₂ = 0.0052 cm⁻¹. The magnetic susceptibility data of the complex [CrLCl₂]₂ shows the expected behaviour of a mononuclear complex. This was confirmed by the EPR spectrum of the compound dissolved in N-methylformamide which is typical for a mononuclear complex with a considerable zero-field splitting.

A very large number of coordination compounds with the diimine ligand H₂salen and its substituted derivatives have been reported1,2 (ligand abbreviations are shown in the Appendix, see also Scheme I). We are currently investigating the much less studied coordination compounds of the corresponding tetrahydrogenated ligand H₂[H₂salen] and its derivatives. We have previously reported the synthesis, crystal structures and properties of

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† To whom correspondence should be addressed.
a series of nickel(II), iron(III), copper(II) and cobalt(II) complexes with the tetrahydrogenated ligands L and L shown in Scheme 1 (in the following L means the negatively charged ligand obtained by dissociation of proton(s) from H₂L, H₂L or HL). As a continuation of these studies an investigation of the corresponding chromium(III) tetrahydroxal complexes was undertaken, and we recently reported the synthesis of a series of novel fluoro-bridged di- and tetrannuclear chromium(III) complexes with the ligands L, L, L, L and L shown in Scheme 1. The complexes were obtained from the reaction of trans-[Cr(pyr)₂F₂]ClO₄ with the corresponding ligand at basic conditions. Two of the complexes, the dinuclear fluoroethoxo-bridged complex: [(CrL₅)₃F(CH₂CH₂O)]H₂O and the tetrannuclear fluoro-bridged complex [Cr₂F₄]., were characterized by single-crystal X-ray structure analysis. In this work we have investigated similar reactions of CrCl₃·6H₂O and trans-[Cr(pyr)₂Cl₂]I and report here the synthesis of three new chromium(III) complexes with these ligands and the crystal structure of the complex with L, [CrLCl]₂.

Experimental

Materials. The compounds H₂L, H₂L, H₂L, and trans-[Cr(pyr)₂Cl₂]I were obtained from methods given in the literature. All other chemicals were of analytical grade.

Analyses. C, H, N and Cl analyses were made by Preben Hansen at the Microanalytical Laboratory at the H. C. Ørsted Institute, Copenhagen.

IR spectra. IR spectra were recorded on a Perkin Elmer System 2000 FTIR spectrometer.

UV–VIS absorption spectra. UV–VIS absorption spectra were obtained using a Cary 3 spectrophotometer.

Mass spectra. FD mass spectra were obtained using a Varian MAT 311 A mass spectrometer. Positive ion FAB mass spectra were obtained on a Jeol AX505W mass spectrometer using NBA (3-nitrobenzylalcohol) as matrix. The m/z values given in the following for chromium(III) complexes and fragments are for the centre of the isotope clusters.

Magnetic measurements. The magnetic moments have been measured with a Faraday balance described elsewhere. The data have been corrected for diamagnetism using Pascal’s constants.

ESR measurements. The ESR spectra have been measured with a Bruker ESP 300 equipped with an Oxford
flow-cryostat ESP 900 (EPR frequency 9.39 GHz, modulation frequency 100 kHz and modulation amplitude 0.5 mT).

Synthesis. For the ligand abbreviations see the Appendix and Scheme 1.

\[ \text{[CrL}^\text{II}]_2 \text{]. NEt}_3 (5 \text{ g, 50 mmol}) \text{ was added to a solution of } \text{H}_2\text{L}^\text{II} (6.81 \text{ g, 25 mmol}) \text{ in 2-methoxethanol (50 ml). Under stirring and heating, a solution of CrCl}_3\cdot6\text{H}_2\text{O (6.66 g, 25 mmol) in 2-methoxethanol (50 ml) and Zn powder (10 mg) was added in one portion. The resulting solution was kept under reflux for 2.5 h. During this time the colour changed to purple, and a blue-green precipitate was formed. The solvent was evaporated in vacuo to 30 ml using a rotary evaporator, and the mixture was allowed to stand overnight at room temperature. The product was filtered off and washed twice with ethanol and then with diethyl ether and dried in the air. This gave 7.1 g of a blue-green powder (79\%\%). M.p. >430°C. Analytical data: Calculated for C_{19}H_{18}N_4O_4CrCl: C, 53.71; H, 5.07; N, 7.82; Cl, 9.91. Found: C, 53.43; H, 5.20; N, 7.62; Cl, 9.88. FABMS m/z = 644 [(CrL)_2]^2. 391 [(CrL}_2\text{Cl}_2]. The complex is sparingly soluble in organic solvents as well as in aqueous acids and bases. It can be dissolved in AgClO_4/HClO_4 or Hg(ClO_4)_2/HClO_4, probably through loss of coordinated chloride.}

Crystals of [CrL}_2\text{Cl}_4] suitable for X-ray structural determination were obtained according to the following procedure: \text{H}_2\text{L}^\text{II} (272 mg, 1 mmol) was dissolved in warm 2-methoxethanol (10 ml, ~40°C). [Cr(py)\text{Cl}_2]I (566 mg, 1 mmol), dissolved in hot 2-methoxethanol (30 ml, ~75°C), was added in one portion. The mixture was heated in an oil bath at 75°C for 48 h without stirring. Then the mixture was allowed to cool slowly to room temperature and was kept at 5°C for 3 d. Finally the product, which contained a number of larger, light blue–green crystals was filtered off, washed several times with ethanol and with diethyl ether and dried over CaCl_2. Yield 170 mg (48\%). IR spectra and X-ray powder diffraction diagrams showed that this complex is identical to the one obtained by the procedure starting with CrCl}_3\cdot6\text{H}_2\text{O.}

\[ \text{[CrL}^\text{III}]_2 \text{. NEt}_3 (1 g, 10 mmol) \text{ was added to a solution of } \text{H}_2\text{L}^\text{III} (1.631 g, 5 mmol) \text{ in 2-methoxethanol (40 ml). Under stirring and heating, a solution of CrCl}_3\cdot6\text{H}_2\text{O (1.332 g, 5 mmol) in 2-methoxethanol (20 ml) and Zn powder (10 mg) was added in one portion. The resulting solution was kept under reflux for 2 h. During this time the colour changed to purple, and a blue precipitate was formed. The solvent volume was reduced to 20 ml by rotary evaporation (60°C), and the mixture was allowed to stand overnight at room temperature. Then the blue product was filtered off and washed twice with ethanol and then with diethyl ether and dried in the air. Yield 1.78 g (86\%). M.p. >430°C. Analytical data: Calculated for C_{19}H_{32}N_2O_4CrCl: C, 58.32; H, 5.87; N, 6.80; Cl, 8.61. Found: C, 57.89; H, 5.94; N, 6.83; Cl, 8.65. FDMS m/z = 822 (M = [CrL}_2\text{Cl}_3], 411 (M/2). FABMS m/z = 822 (M), 787 (M–Cl). The complex is soluble in dimethyl formamide, dimethyl sulfoxide and chloroform.

\[ \text{[CrL}^\text{III}]_2 \text{. NEt}_3 (296 mg, 2.95 mmol) \text{ was added to a solution of HL}^\text{II} (1.09 g, 2.95 mmol) \text{ in 2-methoxethanol (40 ml). With stirring and heating, a solution of CrCl}_3\cdot6\text{H}_2\text{O (787 mg, 2.95 mmol) in 2-methoxethanol (20 ml) and Zn powder (10 mg) was added. The resulting solution was boiled under reflux for 2 h. During this time the colour changed to brown, and a blue precipitate was formed. The mixture was allowed to stand at 5°C overnight. The blue product was filtered off and washed twice with ethanol and then with diethyl ether and dried in the air. Yield 290 mg (20\%). M.p. 320°C (decomp.). Analytical data: Calculated for C_{25}H_{32}N_4O_4CrCl: C, 56.21; H, 6.97; N, 8.55; Cl, 14.43. Found: C, 56.05; H, 7.05; N, 8.54; Cl, 14.52. FDMS m/z = 490 (M = [CrL}_2\text{Cl}_3]. FABMS m/z = 490 (M), 455 (M–Cl). The complex is soluble in dimethyl formamide, acetone and chloroform.

Crystal structure of [CrL}_2\text{Cl}_4]. Crystal data and parameters of the data collection are compiled in Table 1. Unit-cell parameters were determined by accurate centring of 25 strong independent reflections by the least-squares method. Reflection intensities were collected at 298 K on an Enraf-Norius CAD4 four-circle diffractometer equipped with a graphite monochromator and using CuKα radiation. Three standard reflections monitored

<table>
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<td>b/Å</td>
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<td>c/Å</td>
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Table 1. Crystal data and a summary of data reduction and structure refinement for [CrL}_2\text{Cl}_4].
Table 2. Positional parameters and equivalent isotropic thermal parameters for [CrLCl]₂.

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<th>z/c</th>
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every hour during data collection showed no intensity loss. The usual corrections were applied. Diffraction absorption correction has been determined by ψ-scans. The structure was solved by the Patterson method using the program SHELXS-86. Anisotropic least-squares refinement was carried out on all non-H atoms using the program CRYSTALS. Positions of H-atoms were calculated except those bonded to the nitrogen atoms, which have been refined isotropically restraining the C–H distances to 1 Å. Scattering factors were taken from literature. A list of calculated and observed structure factors as well as anisotropic temperature factors is available from the authors. Final positional parameters are given in Table 2, and selected bond lengths and angles are given in Table 3.

Results and discussion

Syntheses. Three new chromium(III) complexes [CrLCl]₂, (L = L¹ or L²) and [CrLCl₂]₂ have been synthesized. The ligands L¹, L² and L⁷, shown in Scheme 1, have been described previously.⁷-⁹ All three chloro complexes were obtained by reaction of CrCl₃·6H₂O and L¹ in 2-methoxyethanol at 124°C with catalytic amounts of zinc and were isolated in high yields (ca. 80% for L¹ and L², whereas the L⁷ complex was isolated only in a yield of 20%). The L¹ complex was also obtained by the reaction of trans-[Cr(py)₄Cl₂] with L¹, also in 2-methoxyethanol. This method gave a smaller yield (48%), but in contrast to the first method, which gave a microcrystalline product, it gave a product consisting of large crystals, which were suitable in size and shape for single-crystal X-ray structure determination (see below).

The stoichiometries of the complexes indicate that they are neutral, so-called inner complexes, and it is therefore not surprising that they all are insoluble or sparingly soluble in neutral aqueous solvents and in most other hydrophilic solvents. The complexes with L¹ and L⁷ were soluble in organic solvents, whereas the compound [CrLCl]₂ was found to be insoluble in all solvents.

Table 3. Selected bond lengths (in Å) and angles (in °) for [CrLCl]₂.

<table>
<thead>
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<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
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<td>Cr(1)–O(1)</td>
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*Atoms with asterisks are symmetry generated.
studied. The general low solubility of the new species made it in practice impossible to characterize and study these new complexes by the classical methods such as pH studies. Data for the visible absorption spectra are given in Table 4, which also includes the infrared (N–H)-stretching vibrations and the coupling constants $J$ calculated from measurements of the magnetic susceptibility (see below).

The similarity of the magnetic properties of the two complexes with $L^1$ and $L^3$ suggest strongly that they are structurally related, and the EPR spectra unambiguously show that they both are dinuclear. We tentatively suggest that the $L^3$ complex has a diphenoxo-bridged structure as found in the crystal structure of the $L^1$ complex (see below). This proposal is substantiated by the observation that the FD mass spectrum of the $L^3$ complex gave intensive signals for the dinuclear species.

The EPR spectrum, the magnetic properties of the $L^7$ complex and the FD mass spectrum provide strong evidence that the complex is mononuclear. The low solubility could be taken as evidence that the complex consists of neutral species, and we therefore presume that both chloride atoms are coordinated to chromium(III).

Descriptions of the crystal structure. The crystals of $[\text{Cr}(\text{L}^1)\text{Cl}]_2$ were thin, blue–green plates. The sample chosen for the X-ray experiment had dimensions of 0.03 × 0.17 × 0.26 mm. The dimeric molecule crystallizes in the orthorhombic space group $Pbc\alpha$. The crystal structure is shown in Figs. 1 and 2. The centroid of the plane formed by the two chromium atoms and the two bridging oxygens of the ligand is situated in the centre of symmetry in 0,0,0, and the dinuclear molecule is therefore a $\text{meso}$-$\Delta,\Delta$ isomer, where $\Delta$ and $\Lambda$ are defined with respect to the two N,O chelates of the $L^1$ ligand (see also Fig. 3). The octahedral coordination polyhedra around the two Cr centres are distorted: all angles deviate significantly from 90°. Whereas the Cr–N distances differ only slightly (2.069 and 2.059 Å), the difference in distance between the Cr atoms and the O atoms is much more pronounced (1.903 and 2.023 Å). The Cr–Cl distance amounts to 2.366 Å. The two Cr(III) centres are bridged by two phenolic O atoms, each belonging to one of the two chelate ligands. The O–Cr–O angle formed by the two phenoxyo bridges is 79.2°, and the Cr–O–Cr angle is 100.8°. The Cr–Cr distance is 3.118 Å.

The diphenoxo-bridged structure is not uncommon in salen chemistry, and has been reported for the complexes $[\text{Fe(salen)Cl}]_2$, $[\text{Cu(salen)}]^{17,18}$ and $[\text{Co(salen)}]^{19,20}$.

\begin{table}[h]
\centering
\caption{Spectroscopic data.}
\begin{tabular}{|l|l|l|l|l|}
\hline
\textbf{Compound} & $\varepsilon,\lambda$ & $\nu_{\text{abs}}/\text{cm}^{-1}$ & $g$ & $J/\text{cm}^{-1}$ \\
\hline
$[\text{Cr}(\text{L}^1)\text{Cl}]_2$ & $-$ & 3214, 3183 & 1.97(1) & 17.1(1) \\
$[\text{Cr}(\text{L}^3)\text{Cl}]_2$ & (144,588) & 3181, 3152 & 1.98(1) & 16.7(1) \\
$[\text{Cr}(\text{L}^3)\text{Cl}]_2$ & (119,580) & 3200 & - & - \\
\hline
\end{tabular}
\label{tab:spectroscopic}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{structure.png}
\caption{Structural view of the coordination geometry of $[\text{Cr}(\text{L}^1)\text{Cl}]_2$.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{numbering.png}
\caption{Numbering scheme for $[\text{Cr}(\text{L}^1)\text{Cl}]_2$.}
\end{figure}

The only structurally characterized Cr(III) salen complex $[\text{Cr(salen)}(\text{H}_2\text{O})_2]\text{Cl}_2$ is monomeric with two water molecules in the axial positions.

\textbf{Magnetic measurements and EPR spectra.} The magnetic susceptibility data of $[\text{Cr}(\text{L}^1)\text{Cl}]_2$ and $[\text{Cr}(\text{L}^3)\text{Cl}]_2$ show that they are weakly coupled antiferromagnetic polynuclear
molecules. The temperature dependence of the magnetic susceptibility of these chloro complexes was measured in the temperature range 4–300 K. The results, which are almost identical for the two species, are shown for [CrL².Cl] for Fig. 4. The susceptibility shows a maximum at approximately 37 K, and the effective magnetic moment declines from 5.2 μB at room temperature to 0.44 μB at 4 K. This is the expected behaviour characteristic for weakly antiferromagnetically coupled dinuclear chromium(III) complexes. For an uncoupled dinuclear chromium(III) complex with g = 2 the expected magnetic moment is 5.9 μB.

The susceptibility of the complex [CrL².Cl] increases on cooling and the magnetic moment decreases from 3.85 μB at room temperature to 2.9 μB at 4 K. This is the expected behaviour of a mononuclear complex.

The temperature dependence of the magnetic susceptibility χ mol,exp was approximated by eqn. (1)

\[
\chi_{\text{mol,exp}} \approx \chi_{\text{mol,calc}} = - \frac{N}{H} \sum_i \frac{\partial E_i}{\partial H} \exp\left(-\frac{E_i}{kT}\right) + K + C/T
\]

by minimization of the term in eqn. (2)

\[
\sum_i \frac{[\chi_{\text{mol,exp}}(T) - \chi_{\text{mol,calc}}(T)]^2}{\sigma'(\chi') + \left(\frac{\partial \chi}{\partial T}\right)^2 \sigma'(T)}
\]

within the framework of nonlinear regression analysis. σ(χ') and σ(T) are the estimated standard deviations on the measured magnetic susceptibility and temperature, respectively. The ratio C/T in eqn. (1) accounts for paramagnetic impurities, and K accounts for temperature-independent paramagnetism and minor deviations in the correction for diamagnetism. The energies E_i of the 16 components of the ground-state manifold were obtained by means of the isotropic spin Hamilton operator, eqn. (3):

\[
\hat{H} = \sum_i g\mu_B \vec{S}_i \cdot \hat{H} + J \vec{S}_1 \cdot \vec{S}_2
\]

where it is assumed that the g values for the two chromium atoms are identical.

The parameters obtained by the minimization for the dinuclear complexes [CrL².Cl] and [CrL².Cl] are g = 1.97(1), J = 17.1(1) cm⁻¹, C = 0.0156 and g = 1.98(1), J = 16.7(1) cm⁻¹, C = 0.0087, respectively. These C-values mean 0.8 and 0.5% impurities, respectively, when interpreted as mononuclear chromium(III) complexes. The

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**Fig. 3.** Schematic drawing of the coordination geometry of Δ,Δ-[CrL².Cl]₂, illustrating the configuration Δ and Δ around the chromium(III) centres (Δ and Δ are defined with respect to the N,O chelates).

**Fig. 4.** The magnetic susceptibility (in c.g.s. units) and the effective magnetic moment of [CrL².Cl] as function of temperature. The lower graph gives the difference between the measured and calculated susceptibilities.

**Fig. 5.** The observed EPR spectrum of a frozen glass of [CrL².Cl], dissolved in N-methylformamide measured at 80 K and at a frequency of 9.39 GHz, and the simulated spectrum. The graph at the bottom gives the angular dependence of the resonance condition, where the ordinate is the angle between the magnetic field and the z-axis of the molecule.
values obtained for $K$ were found to be very small. Calculations using a tetraneuronal model also gave well-defined parameters, so it is not possible from the susceptibility data alone to determine whether the complexes are di- or tetraneuronal. However, from the EPR spectra it can unambiguously be shown that the complex with $L^3$ is dinuclear (see below).

**EPR spectra.** The complexes [CrLCl]$_2$ and [CrLCl]$_2$ are not sufficiently magnetically diluted in the solid state to give well resolved EPR spectra even at 4 K. Only a broad uncharacteristic band centred around $g = 2$ was observed. However, the compound [CrLCl]$_2$ is soluble in N-methylformamide, and the spectrum of this solution measured at 80 K is shown in Fig. 5. This is a typical spectrum from the quintet state which emerges as a result of the antiferromagnetic coupling of the two chromium(III) ions in the dinuclear complex. The spectrum was simulated by means of the spin Hamilton operator given in eqn. (4), where $H_a$ is given by eqn. (5) and $H_a$ by eqn. (6), with a similar Hamilton operator for atom $b$.

It has been assumed that the $g$ values for the two chromium atoms are identical.

$$H = H_a + H_b + H_{ex}$$

$$H_{ex} = J S_a S_b + D_x (2S_a S_{xy} - S_{ax} S_{by} - S_{ay} S_{bx})$$

$$+ E_x (S_{ax} S_{by} - S_{ay} S_{bx})$$

$$H_a = g \mu_B S_a \cdot \mathbf{A} + D_x (2S_a - 1/3 S_a (S_a + 1))$$

$$+ E_x (S_{ax}^2 - S_{ay}^2)$$

The EPR spectrum in Fig. 5 was simulated with the parameters $g = 1.98$, $J = 16.7$ cm$^{-1}$, $D_x = 0.061$ cm$^{-1}$ and $E_x = 0.0052$ cm$^{-1}$. The agreement between the measured and simulated spectrum is not perfect, mainly because we could not determine the mononuclear zfs (zero field splitting) parameters. This has been done previously by using a similar dinuclear complex where one of the two metal atoms is substituted with a diamagnetic metal atom, e.g. cobalt(III). This technique could not be used here since the mixed cobalt(III)–chromium(III) compounds are not known so far. To help interpreting the spectrum the angular dependence of the resonance condition is also shown in Fig. 5. The simulation of ESR spectra of dinuclear chromium(III) complexes has been discussed elsewhere.

The solid-state EPR spectrum of [CrLCl]$_2$ shows a broad line around $g = 2$. The spectrum of the compound dissolved in N-methylformamide is typical for a mononuclear complex with a considerable zfs. Such complexes have been discussed previously.

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**Appendix**

The following ligand abbreviations have been used, see also Scheme 1.

- cis-chxn = cis-1,2-cyclohexanediamine
- trans-(S,S)-chxn = trans-(S,S)-1,2-cyclohexanediamine
- H$_2$salen = N,N’-bis(2-hydroxybenzylidene)-1,2-ethanediame
- H$_2$L$^3$ = tetrahydrosalen = H$_2$[H$_2$salen = N,N’-bis(2-hydroxybenzyl)-1,2-ethanediame
- H$_2$L$^3$ = N,N’-bis(3-tert-butyl-2-hydroxy-5-methylbenzyl)-1,2-ethanediame
- H$_2$L$^4$ = N,N’-bis(2-hydroxybenzyl)-trans-(S,S)-1,2-cyclohexanediamine
- H$_2$L$^4$ = N,N’-bis(3-tert-butyl-2-hydroxy-5-methylbenzyl)-trans-(S,S)-1,2-cyclohexanediamine
- H$_2'L = N,N’-bis(3-tert-butyl-2-hydroxy-5-methylbenzyl)-cis-1,2-cyclohexanediamine
- H$_2'L = N,N’-bis(3-tert-butyl-2-hydroxy-5-methylbenzyl)-cis-1,2-cyclohexanediamine
- H$_2'L = N,N’-bis(3-tert-butyl-2-hydroxy-5-methylbenzyl)-N’ -(1-(2-pyridyl)ethyl)-1,1-dimethyl-1,2-ethanediame

**References**


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