

Diethanolaminium *cyclo*-octa- μ_2 -fluoro-hexadeca- μ_2 -trimethylacetato- κ^{32} O:O'-heptachromium(III)nickel(II) ethyl acetate 0.5-solvate

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Key indicators

Single-crystal X-ray study
 $T = 100$ K
 Mean $\sigma(\text{C}-\text{C}) = 0.007$ Å
 Some non-H atoms missing
 Disorder in main residue
 R factor = 0.089
 wR factor = 0.255
 Data-to-parameter ratio = 35.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $[\text{N}(\text{C}_2\text{H}_4\text{OH})_2\text{H}_2][\text{Cr}_7\text{NiF}_8(\text{C}_5\text{H}_9\text{O}_2)_{16}] \cdot 0.5\text{C}_4\text{H}_8\text{O}_2$, is a heterometallic wheel templated by a protonated amino alcohol. It consists of an octagon of metal centres, with each edge of the octagon bridged by a single F^- anion and two carboxylate groups. Each metal atom is octahedrally coordinated. The protonated amine molecule protrudes through the cavity of the ring, while a solvent ethyl acetate molecule fills up the vacant space between the ring anions. It appears that the one equivalent of Ni atoms is unevenly distributed among the eight metal sites.

Comment

Our recent report (Larsen, McInnes *et al.*, 2003) of a series of octanuclear $\{\text{Cr}_7M\}$ heterometallic wheel-type complexes with the general formula $[\text{NR}_2\text{H}_2][\text{Cr}_7\text{MF}_8(\text{O}_2\text{CCMe}_3)_{16}]$ was the first report of anti-ferromagnetically coupled cyclic molecules that have a non-diamagnetic ground state. There has been considerable interest in such molecules for applications as diverse as olefin polymerization catalysis (Lassahn *et al.*, 2004), magnetic cooling (Affronte *et al.*, 2004) and quantum computing (Meier *et al.*, 2003). They were synthesized using a secondary ammonium cation, $[\text{NR}_2\text{H}_2]^+$, which is a protonated alkyl-chain secondary amine with $R = \text{CH}_3(\text{CH}_2)_n$ (*e.g.* $n = 0-7$). It acts as a template in the reaction of $\text{CrF}_3 \cdot 4\text{H}_2\text{O}$ with pivalic acid in the presence of a second divalent metal cation ($M^{2+} = \text{Ni}, \text{Co}, \text{Mn}, \text{Fe}, \text{Zn}$ or Cd). This procedure gives $\{\text{Cr}_7M\}$ ring compounds in good yield (Larsen, Overgaard *et al.*, 2003; Larsen, McInnes *et al.*, 2003). In each case, the amines are found to be hydrogen-bonded at the centre of the metal ring. The protonated N atoms are not involved in the packing of the molecules in the crystal structure, because they are accommodated completely in the cavity (void) of the wheels. However, it was found that the choice of R can influence the packing of the rings in the crystal structure, regardless of the solvent used for crystallization. For example, both short and very long alkyl chains lead to packing where the octanuclear wheels are coplanar (generally tetragonal or orthorhombic crystals), but for intermediate chain lengths (Et or n Pr), monoclinic crystals are found, where the rings pack with an angle of *ca* 50° between the mean planes of neighbouring rings (Larsen, Overgaard *et al.*, 2003).

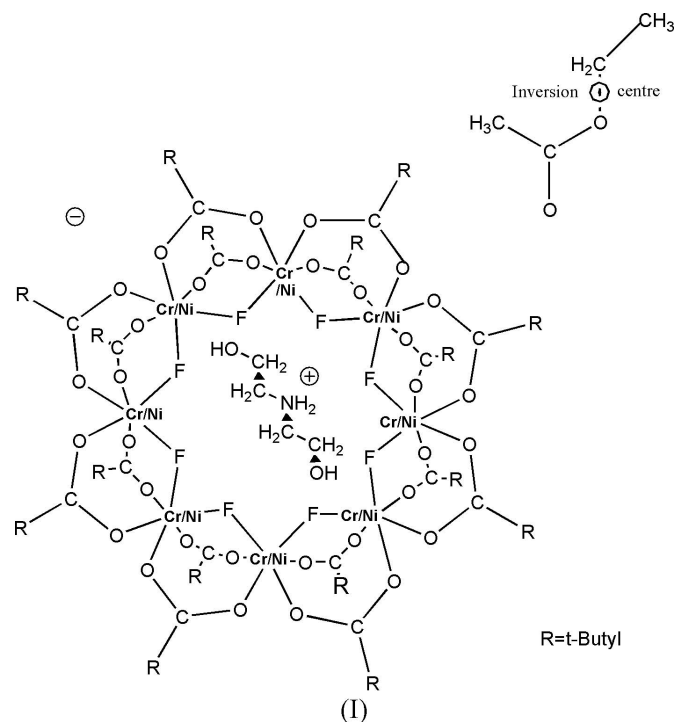
The purpose of this paper is to extend further our studies of heterometallic wheels, by the preparation and structural characterization of the new title complex, $[\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2\text{H}_2][\text{Cr}_7\text{NiF}_8(\text{O}_2\text{CCMe}_3)_{16}][\text{C}_4\text{H}_8\text{O}_2]_{0.5}$, (I). Using a protonated secondary amino alcohol as a template, we wished to investigate the influence of the alcohol group on the accommodation of the amine group in the void of the wheel, and also how the $-\text{OH}$ group might influence the packing of

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the anionic rings in the crystal structure. A further goal was to obtain a complex for the synthesis of further polymetallic cage complexes, using the two OH groups of the diethanolamine to bind to further metal centres.



For five of the 16 bridging pivalate groups in (I), two possible positions were located and refined for the *tert*-butyl methyl groups. The occupation factors for the major component of these five disordered pivalate groups, of which two are on either face, while one is on the edge of the circular ring molecule, are in the range 0.521 (10)–0.592 (9). For all pivalate groups, a restraint was imposed in order to maintain tetrahedral coordination of the CMe₃ groups, and a common C–C bond length was restrained to 1.521 (1) Å.

Compound (I) was crystallized from an ethyl acetate solution and a molecule of ethyl acetate is incorporated in the crystal structure. It is situated near a centre of symmetry and is disordered over two positions, with two of the atom positions coinciding. The protonated ethanolamine molecule appears to be disordered over three orientations in the void of the octagonal ring, with one major [0.444 (5)] and two minor [0.251 (5) and 0.302 (5)] orientations. The amine N atom of the main component sits significantly closer to one side of the ring than the other. The N···F distances vary systematically around the ring: N1···F1 = 3.104 (3), N1···F2 = 3.408 (3), N1···F3 = 3.730 (3), N1···F4 = 3.829 (3), N1···F5 = 3.557 (3), N1···F6 = 3.215 (3), N1···F7 = 2.878 (3) and N1···F8 = 2.855 (3) Å.

In the final cycles of refinement, all Cr/Ni atoms were refined using Cr scattering factors. The metal atoms on the side of the ring with the shorter N···F separations tend to have smaller values for their equivalent isotropic displacement

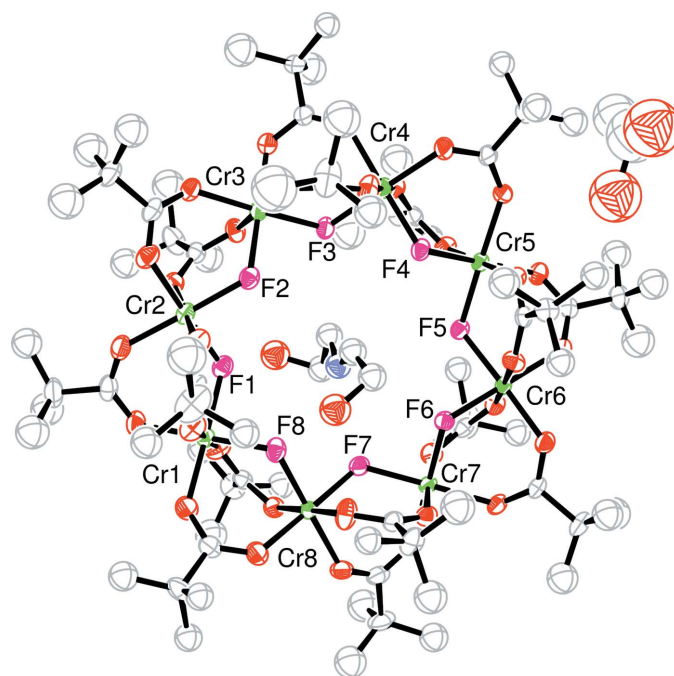


Figure 1

A view of (I), showing 50% displacement ellipsoids, with selected atoms labelled. Only one orientation is shown for the disorder components. Colour key: Cr/Ni green, F pink, O red, C grey, N blue. H atoms have been omitted.

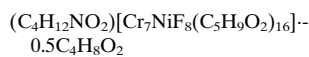
parameters: $U_{eq}(\text{Cr1}) = 0.0238$ (1), $U_{eq}(\text{Cr2}) = 0.0281$ (1), $U_{eq}(\text{Cr3}) = 0.0286$ (1), $U_{eq}(\text{Cr4}) = 0.0308$ (1), $U_{eq}(\text{Cr5}) = 0.0234$ (1), $U_{eq}(\text{Cr6}) = 0.0222$ (1), $U_{eq}(\text{Cr7}) = 0.0238$ (1) and $U_{eq}(\text{Cr8}) = 0.0257$ (1) Å². Since Ni has four more electrons than Cr, it is conceivable that the Cr atoms with lower U_{eq} values may have greater Ni occupancy, so there is an indication of an uneven distribution of Ni around the ring.

The O atoms of the ethanolamine molecule are found to have short distances to the same F atoms which are involved in the shortest N···F separation [O2A···F1 = 2.952 (3) and O2B···F8 = 2.933 (3) Å]. The minor disorder components of the ethanolammonium cation show short N···F distances to other F atoms than found for the major component and of similar lengths: N1C···F1 = 2.721 (3), N1C···F2 = 2.922 (3) and N1C···F8 = 2.939 (3) Å, and N1E···F6 = 2.837 (3), N1E···F7 = 2.940 (3) and N1E···F5 = 3.084 (3) Å.

Experimental

Compound (I) was synthesized in approximately 65% yield in a similar way to the analogues reported earlier (Larsen, Overgaard *et al.*, 2003), except that the amine used was diethanolamine and the product was crystallized from ethyl acetate. Elemental analysis (dried sample), calculated for C₈₄H₁₅₆Cr₇F₈N₁Ni₁O₃₄: Cr 15.83, Ni 2.55, C 43.89, H 6.84, N 0.61%; found: Cr 15.28, Ni 2.72, C 43.89, H 7.00, N 0.62%. ES–MS (2 THF/MeOH *m/z*): –2191 [Cr₇NiF₈(O₂CMe₃)₁₆], 2298 [*M*[–]], 2321 [*M*+Na]⁺.

Crystal data

 $M_r = 2342.85$ Monoclinic, $P2_1/c$ $a = 24.9892$ (15) Å $b = 16.6220$ (9) Å $c = 30.8299$ (19) Å $\beta = 110.506$ (3)° $V = 11994.4$ (12) Å³ $Z = 4$ $D_x = 1.294$ Mg m⁻³Mo $K\alpha$ radiation

Cell parameters from 9946

reflections

 $\theta = 2.2$ – 31.0 ° $\mu = 0.78$ mm⁻¹ $T = 100$ (2) K

Block, green

 $0.38 \times 0.3 \times 0.25$ mm

Data collection

Bruker X8 APEX-II diffractometer
 φ and ω scansAbsorption correction: multi-scan
(*SADABS*; Sheldrick, 1996) $T_{\min} = 0.723$, $T_{\max} = 0.823$

209153 measured reflections

38517 independent reflections

28754 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.035$ $\theta_{\text{max}} = 31.1$ ° $h = -36 \rightarrow 35$ $k = -23 \rightarrow 24$ $l = -44 \rightarrow 44$

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.091$ $wR(F^2) = 0.258$ $S = 1.04$

38517 reflections

1066 parameters

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.1134P)^2 + 52.1149P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} = 0.006$ $\Delta\rho_{\text{max}} = 2.10$ e Å⁻³ $\Delta\rho_{\text{min}} = -1.17$ e Å⁻³

Methyl H atoms were located in idealized positions, with C–H = 0.98 Å, and refined as riding, with the constraint $U_{\text{iso}}(\text{H}) = 1.5U_{\text{iso}}(\text{C})$. N-bound H atoms were located in idealized positions, with N–H = 0.92 Å, and refined as riding, with the constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{N})$.

The highest difference peak is 0.39 Å from H20C and the deepest difference hole is 0.51 Å from C28.

Data collection: *APEX-II* (Bruker–Nonius, 2004); cell refinement: *SAINT-Plus* (Bruker–Nonius, 2004); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *enCIFer* (Version 1.1; Allen *et al.*, 2004) and *WinGX* (Version 1.70.00; Farrugia, 1999).

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