3154 reflections
262 parameters
H atoms not refined
$w = 1/[\sigma^2(F) + (0.030F)^2 + 1.0] - F$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Ni—Cl1	2.302 (1)	N2—C7	1.498 (5)
Ni—N1	2.108 (3)	N2—C18	1.493 (6)
Ni—N2	2.081 (3)	N3—C9	1.487 (5)
Ni—N3	2.088 (3)	N3—C10	1.470 (5)
Ni—N4	2.074 (3)	N3—C16	1.492 (7)
N1—C1	1.338 (5)	N4—C11	1.334 (6)
N1—C5	1.335 (5)	N4—C15	1.343 (5)
N2—C6	1.464 (7)		
Cl1—Ni—N1	101.4 (2)	Ni—N1—C1	130.4 (3)
Cl1—Ni—N2	98.7 (2)	Ni—N1—C5	111.6 (3)
Cl1—Ni—N3	104.1 (1)	Ni—N2—C6	105.6 (4)
Cl1—Ni—N4	99.2 (2)	Ni—N2—C7	114.7 (3)
N1—Ni—N2	80.3 (1)	Ni—N2—C18	104.6 (2)
N1—Ni—N3	152.7 (1)	Ni—N3—C9	114.6 (4)
N1—Ni—N4	104.2 (1)	Ni—N3—C10	107.6 (3)
N2—Ni—N3	86.2 (1)	Ni—N3—C16	103.9 (3)
N2—Ni—N4	160.3 (2)	Ni—N4—C11	113.7 (2)
N3—Ni—N4	81.4 (1)	Ni—N4—C15	128.6 (3)

The title structure was solved by Patterson and difference Fourier methods and refined by full-matrix least-squares methods. H atoms were located and added to the structure-factor calculations, but their positions were not refined.

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual.* Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1060). Services for accessing these data are described at the back of the journal.

References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
Alexander, V. (1995). *Chem. Rev.* **95**, 273–341.
Billman, J. H. & Dorman, L. C. (1962). *J. Org. Chem.* **27**, 2419–2422.
Bu, X.-H., Cao, X.-C., Zhang, W.-Q., Zhang, R.-H. & Clifford, T. (1997). *Transition Met. Chem.* **22**, 513–515.
Buhle, E. L., Moore, A. M. & Wiselogle, F. Y. (1943). *J. Am. Chem. Soc.* **65**, 29–32.
Enraf–Nonius (1977). *CAD-4 Operations Manual.* Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Martin, L. Y., DeHayes, L. J., Zompa, L. J. & Busch, D. H. (1974). *J. Am. Chem. Soc.* **96**, 4046–4048.
Norante, G. de M., Vaira, M. D., Mani, F., Mazzi, S. & Stoppioni, P. (1990). *Inorg. Chem.* **29**, 2822–2829.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

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[1,4,7-Tris(3-*tert*-butyl-5-methyl-2-hydroxybenzyl)-1,4,7-triazacyclononanato-*N*,*N*′,*N*″,*O*,*O*′,*O*″]chromium(III)†

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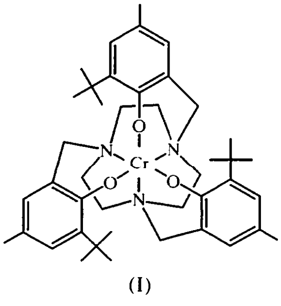
Abstract

The structure analysis of the title compound, $[Cr(C_{42}H_{60}N_3O_3)]$, shows the hexadentate ligand to be coordinated to Cr^{III} in a distorted octahedral arrangement, with the Cr atom situated on a crystallographic threefold axis. Cr—N distances are 2.109 (2) Å and Cr—O distances 1.919 (3) Å.

Comment

During a continuing investigation of the structure–mechanism–function relationship for a number of metalloenzymes, we have explored reactions involving coordinated phenolates. In particular, we are challenged by defining the role of molybdenum in the iron–molybdenum cofactor (FeMoco) in nitrogenase (Steifel *et al.*, 1993). The X-ray structural analysis of FeMoco (Kim & Rees, 1992) identifies the organic ligand, homocitrate, coordinated through two O atoms to the molybdenum. This ligand has been shown to be essential for enzyme function, however, its functional role remains elusive.

In order to define the relationship between the molybdenum centre, the homocitrate ligand and the nitrogenase function, we have prepared the title complex, (I), as a model system for FeMoco. Chromium has been selected as the 'electronic' mimic for molybdenum in these 'first-generation' model complexes and the donor atoms for the bio-mimetic model complex are N_3O_3.



(I)

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† Alternative name: [2,2′,2″-(1,4,7-triazacyclononane-1,4,7-triyl-κ^3N)-tris(6-*tert*-butyl-4-methylphenolato-*O*)]chromium(III).

The Cr^{III} ion lies on a threefold axis and is coordinated to three N atoms and three deprotonated phenolate O atoms (Fig. 1). The hexadentate coordination of the phenolate ligand encapsulates the metal ion thereby reproducing some of the protective character of the protein. The stereochemistry about chromium is distorted from a regular octahedron to meet the steric requirements of the ligand, with three symmetrically equivalent N—Cr—N angles of 82.28 (8)° and O—Cr—O angles of 93.41 (9)°. Cr^{III} complexes of closely related ligands, *e.g.* [1,4,7-tris(5-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononanato-*N*,*N*′,*N*″,*O*,*O*′,*O*″]chromium(III) [Cr—N 2.083 (5) and Cr—O 1.937 (5) Å; Auerbach *et al.*, 1993] and [1,4,7-tris(3-*tert*-butyl-5-methoxy-2-hydroxybenzyl)-1,4,7-triazacyclononanato-*N*,*N*′,*N*″,*O*,*O*′,*O*″]chromium(III) [Cr—N 2.100 (4) and Cr—O 1.920 (3) Å; Sokolowski *et al.*, 1996], show close structural similarity to the title compound. Both of these complexes also exhibit crystallographic threefold symmetry, but crystallize in different space groups. The packing of molecules around the $\bar{3}$ axis is shown in Fig. 2.

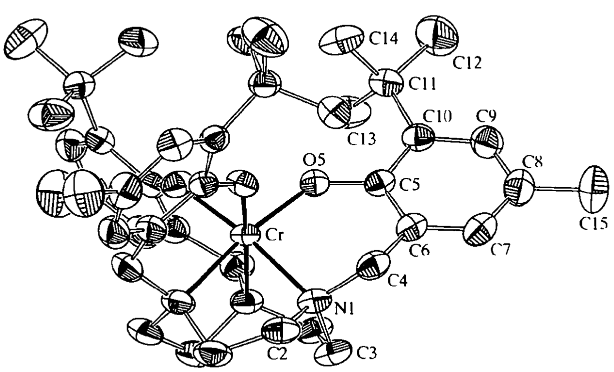

Fig. 1. The title compound shown with 50% displacement ellipsoids. The threefold axis is vertical and H atoms have been omitted.

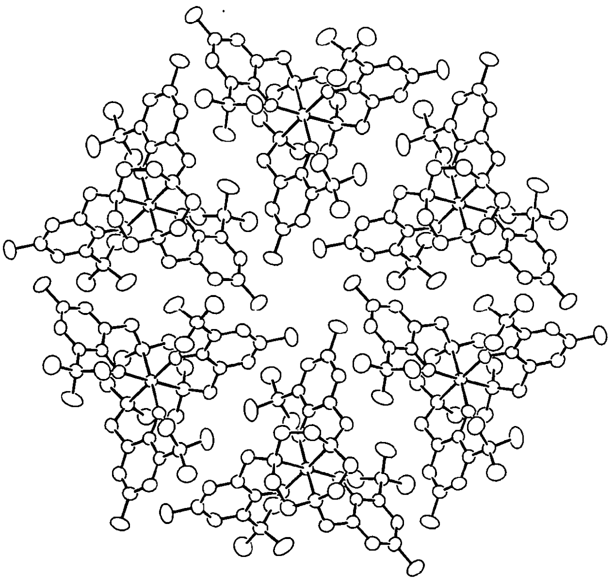

Fig. 2. A view of the structure in projection along **c**, showing the packing of molecules around the $\bar{3}$ axis.

Experimental

The title compound was prepared by dissolving 1,4,7-tris(3-*tert*-butyl-5-methyl-2-hydroxybenzyl)-1,4,7-triazacyclononane in dry acetonitrile with stirring under a nitrogen atmosphere. A stoichiometric amount of $CrCl_2$ was added to this solution and it was heated to reflux for 30 min. The dark green solution was then exposed to the air and after 20 h at room temperature, microcrystals of the required product were obtained. Recrystallization from acetonitrile provided crystals of suitable quality for X-ray structure determination.

Crystal data

$[Cr(C_{42}H_{60}N_3O_3)]$
$M_r = 706.95$
Trigonal
$P\bar{3}$
$a = 14.936\ (1)$ Å
$c = 9.913\ (1)$ Å
$V = 1915.2\ (3)$ Å^3
$Z = 2$
$D_x = 1.226$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15.46$–$18.78°$
$\mu = 0.34$ mm^{-1}
$T = 293$ K
Hexagonal needle
0.46 × 0.24 × 0.18 mm
Deep purple

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: by integration (Davenport *et al.*, 1995)
$T_{min} = 0.930$, $T_{max} = 0.947$
5888 measured reflections
2785 independent reflections
2547 reflections with $F^2 > 0$

$R_{int} = 0.036$
$\theta_{max} = 26.97°$
$h = -19 \rightarrow 0$
$k = 0 \rightarrow 19$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: <1%

Refinement

Refinement on F^2
$R(F) = 0.062$
$wR(F^2) = 0.091$
$S = 1.247$
2547 reflections
228 parameters
All H-atom parameters refined

$w = 1/\sigma^2(F^2)$
$(\Delta/\sigma)_{max} = 0.0003$
$\Delta\rho_{max} = 0.389$ e Å^{-3}
$\Delta\rho_{min} = -0.579$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cr	1/3	2/3	0.08175 (5)	0.0336 (2)
N1	0.21352 (14)	0.57949 (14)	−0.05662 (15)	0.0414 (8)
C2	0.1870 (2)	0.6549 (2)	−0.1162 (2)	0.0499 (12)
C3	0.2484 (2)	0.5318 (2)	−0.1622 (2)	0.0531 (13)
C4	0.12105 (18)	0.49890 (19)	0.0170 (2)	0.0433 (11)

C5	0.21660 (16)	0.44953 (16)	0.18609 (18)	0.0353 (9)
O5	0.29759 (11)	0.54532 (10)	0.18667 (12)	0.0379 (7)
C6	0.13424 (16)	0.41969 (17)	0.0945 (2)	0.0391 (10)
C7	0.05436 (18)	0.31702 (19)	0.0887 (2)	0.0477 (12)
C8	0.05106 (18)	0.24283 (18)	0.1742 (2)	0.0498 (12)
C9	0.1300 (2)	0.27397 (18)	0.2676 (2)	0.0473 (12)
C10	0.21287 (16)	0.37532 (16)	0.2781 (2)	0.0379 (10)
C11	0.29367 (17)	0.40588 (17)	0.3905 (2)	0.0418 (10)
C12	0.2707 (3)	0.3151 (3)	0.4841 (4)	0.078 (2)
C13	0.4016 (2)	0.4457 (3)	0.3311 (3)	0.0703 (17)
C14	0.2939 (3)	0.4903 (3)	0.4773 (3)	0.0631 (16)
C15	−0.0375 (3)	0.1317 (2)	0.1690 (5)	0.075 (2)

Table 2. *Selected geometric parameters (Å, °)*

Cr—N1	2.109 (2)	C6—C7	1.396 (3)
Cr—O5	1.919 (3)	C7—C8	1.376 (4)
N1—C2	1.490 (4)	C8—C9	1.384 (4)
N1—C3	1.499 (4)	C8—C15	1.521 (3)
N1—C4	1.492 (2)	C9—C10	1.400 (3)
C2—C3^{i}	1.512 (4)	C10—C11	1.535 (3)
C4—C6	1.504 (4)	C11—C12	1.534 (5)
C5—O5	1.334 (2)	C11—C13	1.530 (4)
C5—C6	1.410 (3)	C11—C14	1.524 (5)
C5—C10	1.415 (3)		
N1—Cr—O5	91.14 (6)	N1—Cr—O5^{i}	92.67 (8)
N1—Cr—N1^{ii}	82.28 (8)	O5—Cr—O5^{ii}	93.41 (9)
N1—Cr—O5^{ii}	172.17 (6)		

Symmetry codes: (i) $-x+y, 1-x, z$; (ii) $1-y, 1+x-y, z$.

The structure was solved by the heavy-atom method. H atoms were located in difference maps, except for some on methyl groups which were calculated geometrically. The crystal structure contains a small solvent-accessible void at $(0,0,\frac{1}{2})$ with a volume of 55 Å^3 (*PLATON*; Spek, 1997). No residual density was found in that area.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *Xtal*3.4 *DIFDAT ADDREF ABSORB SORTRF* (Hall *et al.*, 1995). Program(s) used to solve structure: *Xtal*3.4. Program(s) used to refine structure: *Xtal*3.4 *CRYLSQ*. Molecular graphics: *Xtal*3.4. Software used to prepare material for publication: *Xtal*3.4 *BONDLA CIFIO*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1214). Services for accessing these data are described at the back of the journal.

References

Auerbach, U., Weyhermuller, T., Weighardt, K., Nuber, B., Bill, E., Butzlaff, C. & Trautwein, A. X. (1993). *Inorg. Chem.* **32**, 508–519.

Davenport, G., Spadaccini, N. & Stewart, J. M. (1995). *ABSORB* in *Xtal*3.4 *Reference Manual*, edited by S. R. Hall, G. S. D. King & J. M. Stewart. Universities of Western Australia, Australia, and Maryland, USA.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Hall, S. R., King, G. S. D. & Stewart, J. M. (1995). Editors. *Xtal*3.4 *Reference Manual*. Universities of Western Australia, Australia, and Maryland, USA.

Kim, J. & Rees, D. C. (1992). *Nature* (*London*), **360**, 553–560.

Sokolowski, A., Bothe, E., Bill, E., Weyhermuller, T. & Weighardt, K. (1996). *Chem. Commun.* pp. 1671–1672.

Spek, A. L. (1997). *PLATON. Molecular Geometry Program*. University of Utrecht, The Netherlands.

Steifel, E. I., Coucouvanis, D. & Newton, W. E. (1993). Editors. *Molybdenum Enzymes, Cofactors and Model Systems. Am. Chem. Soc. Symp. Ser.* No. 535.

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Cobalt(II) complexes of piperazine and derivatives: 1-methylpiperazin-4-ium trichloro(1-methylpiperazine-N^4)cobaltate(II)

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Abstract

The title compound, $(C_5H_{13}N_2)[CoCl_3(C_5H_{12}N_2)]$, contains a Co^{II} ion coordinated to three Cl atoms and to the unmethylated N atom of *N*-methylpiperazine in a distorted tetrahedral geometry. The six-membered ring of both the coordinated and free *N*-methylpiperazine molecules possesses the more stable chair conformation. In addition, other tautomeric forms may be present in small amounts in the crystals.

Comment

Piperazine (H$_2$ppz) is a cyclic 1,4-diamine that can coordinate metal ions as a monodentate, bidentate or bidentate–chelate ligand. The last form is very rare because the piperazine ring must assume the boat conformation, which is 17.2 kJ mol^{-1} less stable than the chair conformation (Niemeyer, 1979). Recently, we have studied several *N*-methylpiperazine (HMeppz) and *N,N'*-dimethylpiperazine (Me$_2$ppz) Pt^{II} complexes (Marzotto *et al.*, 1997, 1998*a*; Ciccarese *et al.*, 1998). A few of them show some antitumour activity, such as the boat chelate *cis*-[PtCl$_2$(Me$_2$ppz)], which resembles cisplatin. In order to gain further insight into the ability of coordination complexes to interact selectively with the N atoms of DNA nucleobases, we have synthesized some tetrahedral Co^{II} complexes containing *N*-methylated piperazine for possible biological applications. We report here the structure of the present compound, (I), mainly constituted by [H$_2$Meppz]$^+$ cations