

For both data sets, unit-cell dimensions were determined from reflections taken from three sets of 30 frames (at 0.3° steps in ω), each at 20 s exposure. Slightly more than a full hemisphere of reciprocal space was scanned by 0.3° ω steps at $\varphi = 0, 90$ and 180° , with the area detector held at $2\theta = -29^\circ$ and each frame exposed for 30 s. The crystal-to-detector distance was 4.94 cm. Crystal decay was monitored by repeating the initial 50 frames at the end of data collection and analysing the duplicate reflections. No decay was observed in either data set. The data sets were corrected empirically for absorption effects and refined by the full-matrix least-squares method on all F^2 data. H atoms were constrained to idealized geometries and each was assigned an isotropic displacement parameter of 1.2 times the U_{eq} value of the attached atom. For $[\text{CuL}_2][\text{ClO}_4]$, one of the three independent perchlorate anions is disordered. Atoms C11 and O14 were fixed, but rotational disorder about this bond resulted in atoms O11, O12 and O13 being each disordered over two sites in a 60:40 ratio. Three of these disordered atom sites (O12, O12' and O13') have rather extreme anisotropic displacement parameters. For $[\text{AgL}_2][\text{BF}_4]$, the largest residual electron-density peak of $1.29 \text{ e } \text{Å}^{-3}$ is located 1.00 Å from Br21.

For both compounds, data collection: *SMART* (Siemens, 1995b); cell refinement: *SAINT* (Siemens, 1995b); data reduction: *SAINT*; program(s) used to solve structures: *SHELXTL* (Siemens, 1995a); program(s) used to refine structures: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We thank the University of Bristol for financial support (SMC).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1374). Services for accessing these data are described at the back of the journal.

References

- Bardwell, D. A., Jeffery, J. C., Otter, C. A. & Ward, M. D. (1996). *Polyhedron*, **15**, 191–194.
- Cargill Thompson, A. M. W., Blandford, I., Redfeam, H., Jeffery, J. C. & Ward, M. D. (1997). *J. Chem. Soc. Dalton Trans.* pp. 2661–2665.
- Desiraju, G. R. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2311–2327.
- Federlin, P., Kern, J.-M., Rastegar, A., Dietrich-Buchecker, C., Marnot, P. A. & Sauvage, J.-P. (1990). *New J. Chem.* **14**, 9–12.
- Geoffroy, M., Wermeille, M., Buchecker, C. O., Sauvage, J.-P. & Bernardinelli, G. (1990). *Inorg. Chim. Acta*, **167**, 157–164.
- Goodwin, K. V., McMillin, D. R. & Robinson, W. R. (1986). *Inorg. Chem.* **25**, 2033–2036.
- Ichinaga, A. K., Kirchoff, J. R., McMillin, D. R., Dietrich-Buchecker, C. O., Marnot, P. A. & Sauvage, J.-P. (1987). *Inorg. Chem.* **26**, 4290–4292.
- Müller, E., Bernardinelli, G. & Reedijk, J. (1996). *Inorg. Chem.* **35**, 1952–1957.
- Pedireddi, V. R., Reddy, D. S., Goud, B. S., Craig, D. C., Rac, A. D. & Desiraju, G. R. (1994). *J. Chem. Soc. Perkin Trans. 2*, pp. 2353–2360.
- Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction*. University of Göttingen, Germany.
- Siemens (1995a). *SHELXTL*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1995b). *SMART and SAINT. Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1998). **C54**, 1823–1825

Aquabis(2,3-butanedione dioximato-*N,N'*)-(cyclopentyl)cobalt(III)

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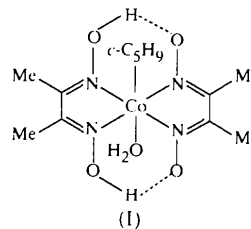
(Received 26 February 1998; accepted 2 July 1998)

Abstract

The crystal structure determination of the title compound, a model for coenzyme B₁₂, indicates that it is $[\text{Co}(\text{C}_4\text{H}_6\text{N}_2\text{O}_2)(\text{C}_5\text{H}_9)(\text{C}_4\text{H}_8\text{N}_2\text{O}_2)(\text{H}_2\text{O})]$, *i.e.* one 2,3-butanedione dioxime ligand is neutral and the second is a dianion, with the Co^{III} ion in a distorted octahedral environment. The axial Co—C bond length [$2.029(2) \text{ Å}$] is close to that of coenzyme B₁₂ [$2.00(1) \text{ Å}$].

Comment

Alkylcobaloximes $[\text{RCo}(\text{DH})_2\text{L}]$; where *DH* is the monoanion of dimethylglyoxime (2,3-butanedione dioxime), *R* is alkyl and *L* is a donor ligand] are a type of widely studied coenzyme B₁₂ models having a σ -type Co—C bond; their structures and properties have been well characterized (Bresciani-Pahor *et al.*, 1985). However, only a few structures of alkylaquacobaloximes (*L* = H₂O) are available and in this paper, we report a new one, that of aquabis(2,3-butanedione dioximato-*N,N'*)-(cyclopentyl)cobalt(III), (I).



An *ORTEP* plot (Johnson, 1965) of the title compound with the atom-numbering scheme is shown in Fig. 1. The Co^{III} ion is coordinated by four N atoms (N1, N2, N3 and N4), a C atom (C1') and an O atom (O1W), forming a distorted octahedral environment. The four N atoms are coplanar. The Co^{III} atom is displaced slightly [$0.030(1) \text{ Å}$] from the N_4 mean plane towards the cyclopentyl group. The dihedral angle between the plane formed by atoms C1–C4, N1, N2, O1, O2 and Co1 (mean deviation from the

best plane is 0.045 Å), and that formed by atoms C5—C8, N3, N4, O3, O4 and Co1 (mean deviation from the best plane is 0.019 Å) is 4.35 (2)°. The two dimethylglyoxime groups are linked by intramolecular hydrogen bonds [O1—H1···O3: O1···O3 2.500 (3) Å and O1—H1···O3 166 (3)°; O2—H2···O4: O2···O4 2.493 (3) Å and O2—H2···O4 145 (3)°]. Thus, both H atoms appear to be attached to the same dimethylglyoxime ligand and the complex is therefore [Co(C₄H₆N₂O₂)(C₅H₉)(C₄H₈N₂O₂)(H₂O)], with one dimethylglyoxime ligand neutral and the second dianionic. This arrangement has occasionally been observed before accompanied, as here, by a small lengthening of the Co—N and N—O distances in the neutral ligand compared with those in the anionic ligand (Bresciani-Pahor *et al.*, 1985).

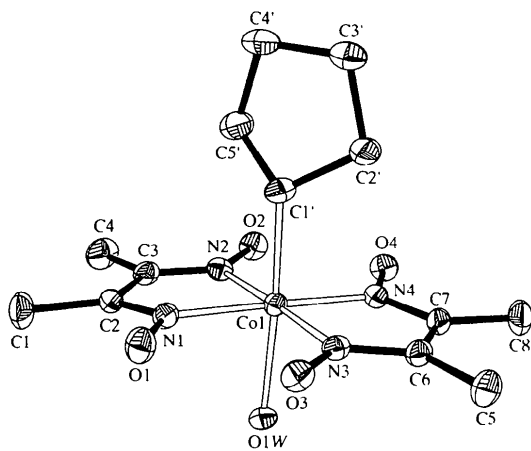


Fig. 1. The molecular structure of (I) showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

Other bond lengths and angles are in agreement with those in related compounds (Bresciani-Pahor *et al.*, 1982, 1985; Savage *et al.*, 1987; Randaccio *et al.*, 1989).

Experimental

The title compound was synthesized according to the method of Toscano *et al.* (1983) and slowly crystallized as dark-red prism-shaped crystals from a methanol–water solution in air.

Crystal data

[Co(C₄H₆N₂O₂)(C₅H₉)-
(C₄H₈N₂O₂)(H₂O)]
M_r = 376.30
Triclinic
P $\bar{1}$

Mo *K*α radiation
λ = 0.71073 Å
Cell parameters from 28
reflections
θ = 4.82–12.52°

a = 9.215 (5) Å
b = 9.607 (8) Å
c = 10.575 (5) Å
α = 113.24 (4)°
β = 91.76 (3)°
γ = 90.84 (5)°
V = 859.5 (9) Å³
Z = 2
D_s = 1.454 Mg m⁻³
D_m not measured

μ = 1.028 mm⁻¹
T = 293 (2) K
Prism
0.50 × 0.35 × 0.20 mm
Red

Data collection

Siemens *P4* diffractometer
2θ/ω scans
Absorption correction:
empirical ψ scan (North
et al., 1968)
T_{min} = 0.631, *T_{max}* = 0.826
3417 measured reflections
2813 independent reflections
1973 reflections with
I > 2σ(*I*)

R_{int} = 0.062
θ_{max} = 25°
h = -1 → 10
k = -10 → 10
l = -12 → 12
3 standard reflections
every 97 reflections
intensity decay: 5.35%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.068
wR(*F*²) = 0.157
S = 0.954
2809 reflections
224 parameters
H atoms riding
w = 1/[σ²(*F_o*²)]

(Δ/σ)_{max} = 0.001
Δρ_{max} = 0.961 e Å⁻³
Δρ_{min} = -0.653 e Å⁻³
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Co1—N4	1.868 (2)	N1—C2	1.289 (3)
Co1—N3	1.875 (2)	N2—C3	1.293 (3)
Co1—N2	1.893 (2)	N3—C6	1.305 (2)
Co1—N1	1.901 (2)	N4—C7	1.306 (2)
Co1—C1'	2.029 (2)	C1'—C5'	1.488 (3)
Co1—O1W	2.087 (2)	C1'—C2'	1.507 (3)
O1—N1	1.356 (3)	C2'—C3'	1.524 (3)
O2—N2	1.357 (3)	C3'—C4'	1.501 (3)
O3—N3	1.348 (2)	C4'—C5'	1.547 (3)
O4—N4	1.349 (2)		
N4—Co1—N3	82.01 (9)	N1—Co1—C1'	88.71 (9)
N4—Co1—N2	98.51 (9)	N4—Co1—O1W	91.11 (8)
N3—Co1—N2	178.11 (7)	N3—Co1—O1W	91.45 (7)
N4—Co1—N1	178.11 (7)	N2—Co1—O1W	86.72 (8)
N3—Co1—N1	98.61 (9)	N1—Co1—O1W	87.08 (8)
N2—Co1—N1	80.82 (9)	C1'—Co1—O1W	175.51 (8)
N4—Co1—C1'	93.11 (9)	C5'—C1'—Co1	117.7 (2)
N3—Co1—C1'	87.65 (9)	C2'—C1'—Co1	119.61 (12)
N2—Co1—C1'	94.14 (9)		

The H atoms of the water molecules and those attached to the glyoxime O atoms were found from the difference Fourier map and refined isotropically. Although inspection of coordinates shows that individual molecules have an approximate mirror plane at $\frac{1}{2}$, this does not persist in the molecular packing and we believe the structure is triclinic, not monoclinic. Refinement as monoclinic was not satisfactory.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: SHELXTL (Siemens, 1995). Program(s) used to solve structure: SHELXTL. Program(s) used to refine structure: SHELXTL. Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL.

This research was supported by the National Nature Science Foundation of China.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1217). Services for accessing these data are described at the back of the journal.

References

- Bresciani-Pahor, N., Forcolin, M., Marzilli, L. G., Randaccio, L., Summers, M. F. & Toscano, P. J. (1985). *Coord. Chem. Rev.* **63**, 1–125.
- Bresciani-Pahor, N., Randaccio, L., Toscano, P. J. & Marzilli, L. G. (1982). *J. Chem. Soc. Dalton Trans.* pp. 567–572.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Randaccio, L., Bresciani-Pahor, N., Zangrando, E. & Marzilli, L. G. (1989). *Chem. Soc. Rev.* **18**, 225–250.
- Savage, H. F. J., Lindley, P. F., Finney, J. L. & Timmins, P. A. (1987). *Acta Cryst.* **B43**, 280–295.
- Siemens (1994). *XSCANS. X-ray Single Crystal Analysis System*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1995). *SHELXTL Reference Manual*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Toscano, P. J., Swider, T. F., Marzilli, L. G., Bresciani-Pahor, N. & Randaccio, L. (1983). *Inorg. Chem.* pp. 3416–3421.

Acta Cryst. (1998). **C54**, 1825–1827

exo- and *endo*-Tricarbonyl[(4b,5,6,7,8,8a- η)-*cis*-*N*-methyl-2,3,4,4a,9,9a-hexahydro-1*H*-carbazole]chromium(0)

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(Received 15 April 1998; accepted 14 July 1998)

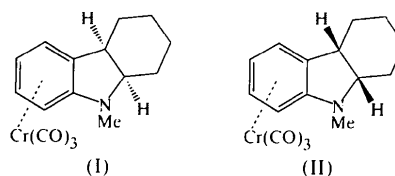
Abstract

Acid-mediated hydride reduction of tricarbonyl(η^6 -*N*-methyl-1,2,3,4-tetrahydrocarbazole)chromium(0) affords either the *cis*-fused *exo*-hexahydrocarbazole–chromium(0) complex $\{[\text{Cr}(\text{C}_{13}\text{H}_{17}\text{N})(\text{CO})_3]\}$, (I) exclusively, or a separable mixture of (I) and the *endo*-isomer $\{[\text{Cr}(\text{C}_{13}\text{H}_{17}\text{N})(\text{CO})_3]\}$, (II), depending upon the choice of hydride donor. The conformations of the hexahydrocarbazole systems differ in the orientation of the indoline moiety with respect to the saturated hexahydrocarbazole rings. The isolation of the *exo*-isomer is un-

usual, as this complex arises *via* reaction at the sterically more hindered *endo* face of the coordinated ligand.

Comment

The chemistry of (η^6 -arene)tricarbonylchromium complexes continues to attract much attention, owing to the multitude of reactions in which the bound arene can participate (Semmelhack, 1995). Moreover, most transformations of chromium-complexed arenes proceed with excellent levels of stereoselectivity, as a consequence of the stereodirecting effect of the $\text{Cr}(\text{CO})_3$ fragment (Davies & McCarthy, 1995). In a study aimed at extending this useful reactivity profile to include stereocontrolled manipulations of η^6 -coordinated indoles, the acid-mediated hydride reduction of (indole) $\text{Cr}(\text{CO})_3$ complexes has been explored (Pigge *et al.*, 1998). It is in connection with this project that the title complexes, (I) and (II), were prepared and structurally characterized.



The molecular structures of (I) and (II) are shown in Figs. 1 and 2, respectively. The exclusive production of the *exo*-isomer, (I), under the initial set of reaction conditions is significant, as this complex results from reaction at the nominally sterically more hindered *endo* face of the coordinated indole ligand. Such *endo*-selective reactions of (arene)chromium complexes have rarely been observed (Sur *et al.*, 1996). It is also noteworthy that (I) and (II) represent two of only a few structurally characterized (η^6 -indoline)–transition metal complexes (Chen *et al.*, 1997; Heaton *et al.*, 1993; Dickens *et al.*, 1989).

Bond distances and angles for the two complexes are quite similar, with the major structural difference being the stereochemistry of the carbazole ring fusion relative to the $\text{Cr}(\text{CO})_3$ group. The average Cr–CO distances are 1.834 (2) and 1.832 (4) Å, and the average OC–Cr–CO angles are 88.16 (9) and 88.04 (8)°, for compounds (I) and (II), respectively. The $\text{Cr}(\text{CO})_3$ fragment adopts a partially eclipsed conformation with the coordinated arene, and the three CO ligands are aligned over C5, C7, and C8a. Such a conformation is typical in $\text{Cr}(\text{CO})_3$ complexes of arenes bearing an electron-releasing substituent (Solladie-Cavallo, 1985). The Cr–C_{arene} distances vary in the ranges 2.202 (2)–2.346 (2) and 2.200 (2)–2.390 (2) Å in (I) and (II), respectively. The distance from the Cr atom to the centroid of the aromatic ring is 1.757 in (I) and 1.773 Å in (II). The bond distances and angles within the aromatic ring itself are typical for both complexes [mean values are 1.410 (3)