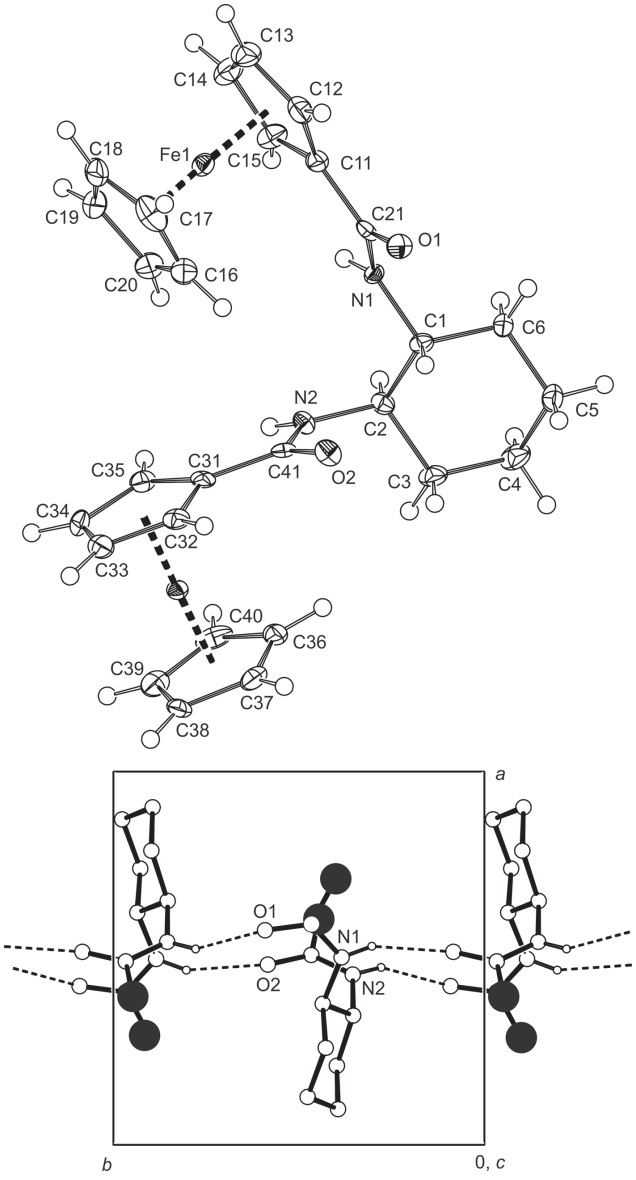
Martin Zábranský, Zdeněk Leitner and Petr Štěpnička*

The crystal structure of (1*R*, 2*R*)-N^1,N^2-diferrocenyl-1,2-cyclohexanedicarboxamide, $C_{28}H_{30}Fe_2N_2O_2$



https://doi.org/10.1515/ncrs-2017-0294
Received October 2, 2017; accepted December 11, 2017; available online January 18, 2018

Abstract

$C_{28}H_{30}Fe_2N_2O_2$, monoclinic, $P2_1$ (no. 4), $a = 10.7490(10)$ Å, $b = 9.8370(8)$ Å, $c = 11.9621(13)$ Å, $\beta = 113.030(4)°$, $V = 1164.04(19)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0358$, $wR_{ref}(F^2) = 0.0612$, Flack parameter $= -0.007(11)$, $T = 150(2)$ K.

CCDC no.: 1590366

The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Bar, orange
Size:	0.27 × 0.07 × 0.07 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.28 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω-scans
θ_{max}, completeness:	28°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13446, 5616, 0.038
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4852
$N(param)_{refined}$:	307
Programs:	SHELX [2, 3], PLATON [4], Bruker programs [5, 6],

Source of material

Ferrocenecarboxylic acid (244 mg, 1.1 mmol) and 1-hydroxybenzotriazole (205 mg, 1.5 mmol) were dissolved in anhydrous dichlormethane (20 mL) by gentle heating in a reaction flask equipped with a stirring bar under an argon atmosphere. The solution was cooled on ice and neat 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide (0.26 mL, 1.5 mmol) was introduced, causing the partly precipitated acid to redissolve. After stirring the mixture at 0 °C for 15 min, a dichloromethane solution of (1*R*, 2*R*)-1,2-diaminocyclohexane (60 mg, 0.50 mmol in 10 mL) was added and the stirring was continued at 0 °C 5 min and then at room

***Corresponding author: Petr Štěpnička,** Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, CZ-12840 Prague, Czech Republic, e-mail: petr.stepnicka@natur.cuni.cz
Martin Zábranský and Zdeněk Leitner: Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, CZ-12840 Prague, Czech Republic

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Fe1	0.88602(5)	0.38170(5)	0.79243(5)	0.01641(13)
Fe2	0.52865(5)	0.43236(5)	0.11877(4)	0.01371(12)
O1	0.5748(2)	0.5912(2)	0.7324(2)	0.0183(6)
O2	0.4830(2)	0.5837(2)	0.3896(2)	0.0194(6)
N1	0.5021(2)	0.3849(3)	0.6469(2)	0.0133(6)
H1N	0.531952	0.303423	0.652044	0.016*
N2	0.4561(3)	0.3549(3)	0.3925(3)	0.0142(7)
H2N	0.475329	0.278465	0.366529	0.017*
C1	0.3777(3)	0.4357(4)	0.5533(3)	0.0144(7)
H1	0.391484	0.533035	0.536812	0.017*
C2	0.3465(3)	0.3537(4)	0.4360(3)	0.0156(8)
H2	0.334878	0.257055	0.455904	0.019*
C3	0.2119(3)	0.3977(4)	0.3366(3)	0.0216(10)
H3A	0.221181	0.491098	0.309923	0.026*
H3B	0.190171	0.336649	0.265659	0.026*
C4	0.0958(3)	0.3944(4)	0.3799(3)	0.0255(10)
H4A	0.013208	0.431305	0.315366	0.031*
H4B	0.077507	0.299044	0.395093	0.031*
C5	0.1282(3)	0.4765(4)	0.4948(4)	0.0225(9)
H5A	0.053605	0.467283	0.523276	0.027*
H5B	0.136505	0.573744	0.477667	0.027*
C6	0.2598(3)	0.4276(5)	0.5939(3)	0.0181(8)
H6A	0.248785	0.332440	0.615304	0.022*
H6B	0.280321	0.484074	0.667504	0.022*
C11	0.7128(3)	0.4004(4)	0.8204(3)	0.0179(9)
C12	0.8204(4)	0.4715(4)	0.9119(3)	0.0224(9)
H12	0.822256	0.566282	0.927844	0.027*
C13	0.9237(4)	0.3778(5)	0.9747(3)	0.0265(10)
H13	1.006472	0.398102	1.040434	0.032*
C14	0.8815(4)	0.2480(4)	0.9222(4)	0.0284(10)
H14	0.931480	0.165972	0.946343	0.034*
C15	0.7519(4)	0.2618(4)	0.8275(4)	0.0212(9)
H15	0.700042	0.190382	0.777329	0.025*
C16	0.8567(4)	0.4890(5)	0.6383(4)	0.0279(10)
H16	0.783432	0.548690	0.597609	0.033*
C17	0.9818(4)	0.5257(4)	0.7319(4)	0.0309(11)
H17	1.007085	0.614127	0.764890	0.037*
C18	1.0621(4)	0.4070(5)	0.7674(3)	0.0297(11)
H18	1.150844	0.401707	0.828668	0.036*
C19	0.9883(4)	0.2989(4)	0.6965(4)	0.0275(10)
H19	1.018325	0.207461	0.701042	0.033*
C20	0.8602(4)	0.3493(4)	0.6165(4)	0.0277(11)
H20	0.789707	0.297562	0.558595	0.033*
C21	0.5910(3)	0.4667(4)	0.7297(3)	0.0146(8)
C31	0.6027(3)	0.4477(4)	0.3020(3)	0.0154(8)
C32	0.6526(4)	0.5572(4)	0.2539(3)	0.0170(9)
H32	0.640052	0.651180	0.264531	0.020*
C33	0.7244(4)	0.5017(4)	0.1876(4)	0.0223(10)
H33	0.766680	0.552230	0.144558	0.027*
C34	0.7224(4)	0.3584(4)	0.1962(4)	0.0215(10)
H34	0.764504	0.296233	0.161145	0.026*
C35	0.6466(4)	0.3236(4)	0.2664(4)	0.0187(9)
H35	0.628304	0.234264	0.286154	0.022*
C36	0.3242(3)	0.4290(5)	0.0631(3)	0.0218(8)
H36	0.275888	0.433541	0.114697	0.026*
C37	0.3625(4)	0.5403(4)	0.0096(4)	0.0215(9)
H37	0.343985	0.633212	0.018562	0.026*
C38	0.4329(4)	0.4905(4)	−0.0593(3)	0.0204(9)
H38	0.471022	0.543687	−0.104229	0.024*
C39	0.4368(4)	0.3484(4)	−0.0498(4)	0.0244(10)
H39	0.477156	0.288360	−0.088109	0.029*
C40	0.3704(4)	0.3096(4)	0.0263(4)	0.0247(10)
H40	0.358958	0.219324	0.048827	0.030*
C41	0.5087(3)	0.4666(4)	0.3652(3)	0.0143(8)

temperature overnight. Then, the reaction mixture was washed with saturated aqueous $NaHCO_3$ and brine (twice each), dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The residue was purified by column chromatography over silica gel using dichloromethane-methanol (20:1) as the eluent. The first minor band containing [(1*H*-benzotriazol-1-yloxy)carbonyl]ferrocene [1] (63 mg, 17%) was followed by a major orange band due to the product. Following evaporation, the title compound was isolated as an orange amorphous solid (216 mg, 76%). Single crystals were grown by slow cooling of a methanolic solution.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ = 1.41 (m, 4 H), 1.83 (m, 2 H) and 2.25 (m, 2 H) (4 × CH_2 of C_6H_{10}), 3.84 (m, 2 H, 2 × CH of C_6H_{10}), 4.09 (s, 10 H, C_5H_5), 4.30 (m, 4 H) and 4.70 (m, 4 H) (4 × CH of C_5H_4), 6.50 (d, $^3J_{HH}$ = 6.8 Hz, 2 H, NH) ppm **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.58 MHz): δ = 24.79 (s, 2 C) and 32.66 (s, 2 C) (4 × CH_2 in C_6H_{10}), 54.27 (s, 2 C, 2 × CH in C_6H_{10}), 68.18 (s, 2 C, CH of C_5H_4), 68.34 (s, 2 C, CH in C_5H_4), 69.73 (s, 10 C, C_5H_5), 70.53 (s, 4 C, CH of C_5H_4), 75.71 (s, 2 C, *C*—CO of C_5H_4), 171.31 (s, 2 C, C=O) ppm **IR** (Nujol): ν_{max} = 3313 (br s, ν(NH)), 3228 (w), 3120 (w), 3096 (w), 3081 (m), 1625 (s, ν(C=O)), 1545 (s, δ(NH)), 1411 (m), 1353 (m), 1344 (m), 1320 (m), 1302 (s), 1273 (m), 1247 (w), 1221 (w), 1184 (m), 1140 (vw), 1108 (m), 1085 (vw), 1048 (vw), 1022 (m), 1015 (m), 1003 (m), 955 (vw), 928 (w), 888 (w), 865 (w), 821 (m), 812 (m), 773 (m), 762 (w), 648 (br w), 608 (vw), 584 (vw), 530 (w), 519 (m), 504 (m), 497 (m), 484 (m), 462 (m), 445 (w), 430 (vw) cm^{-1}. **MS** (ESI+): *m/z* = 561.1 ($[M + Na]^+$). Anal. Calc. for $C_{28}H_{30}Fe_2N_2O_2$ (538.24 g·mol^{-1}): C 62.48, H 5.62, N 5.21%. Found: C 62.15, H 5.68, N 5.04%.

Experimental details

The structure was solved by Direct methods using SHELXS-97 [2] and then refined by least-squares routine based on F^2 (SHELXL-2017 [3]). Hydrogen atoms attached to nitrogen atoms were identified on the difference electron density maps and refined as riding atoms with U_{iso}(H) = 1.2 U_{eq}(N) [3]. All other hydrogen atoms were included in their calculated

positions with $U_{iso}(H) = 1.2\ U_{eq}(C)$. The structural drawing and all numerical parameters discussed below were obtained with a recent version of the PLATON program [4]. The absolute configuration determined by anomalous dispersion [7] corresponded to that declared for the starting diamine (*cf.* Table 1).

Discussion

Carboxamides obtained from chiral diamines and phosphinocarboxylic acids emerged as efficient auxiliary ligands for a range enantioselective transition-metal catalyzed reactions [8]. In the chemistry of ferrocene-based ligands, compounds of this type are represented by amides obtained from 1,2-diaminocyclohexanes and planar-chiral 2-(diphenylphosphino)ferrocene-1-carboxylic acid [8–10]. Because none of these compound appears to have been structurally characterized, we decided to synthesize and characterize an analogous compound without the phosphine substituents at the ferrocene moieties, *viz*. (1*R*, 2*R*)-N^1,N^2-diferrocenyl-1,2-cyclohexanedicarboxamide. This compound was prepared by amidation of (1*R*, 2*R*)-diaminocyclohexane with ferrocenecarboxylic acid in the presence of peptide coupling agents [11] and was isolated as an orange solid in 76% yield by column chromatography. Chromatographic purification also afforded some [(1*H*-benzotriazol-1-yloxy)carbonyl]ferrocene, representing a non-consumed reaction intermediate.

The compound crystallizes in the non-centrosymmetric space group $P2_1$ and two molecules in the unit cell. The central six-membered ring in each dinuclear title complex has a chair conformation, which is manifested by the ring puckering coordinate θ [12] being 176.7(4)° (Note: ideal chair requires θ = 0° or 180°). The pivotal C—N bonds occupy equatorial positions and their length (C1—N1 = 1.456(4) Å, C2—N2 = 1.462(5) Å) as well as the N1—C21—C2—N2 torsion angle of −56.2(4)° are similar to those in the parent amine, (1*R*, 2*R*)-diaminocyclohexane [1.465(2) Å and −59.2(1)°, respectively] [13].

The ferrocene moieties in the title compound adopt the usual geometry with the individual Fe—C distances falling into narrow ranges, 2.025(4) Å (C11) to 2.056(3) Å (C13), and 2.024(3) Å (C31) to 2.053(5) Å (C33) for the ferrocene units comprising Fe1 and Fe2, respectively. Correspondingly, the dihedral angles subtended by the least-squares planes of the cyclopentadienyl rings are only 3.2(3)° (Fe1) and 3.7(3)° (Fe2). Even so, the amide substituents are rotated only slightly from the planes of their bonding cyclopentadienyl rings. In this case, however, a smaller departure from a coplanar arrangement is observed for the ferrocene unit comprising atom Fe1 that for the other ferrocene moiety (compare the angle between the {C21, N1, O1} and C(11—15) planes of 4.2(4)° with that subteneded by the planes {C41, N2, O2} and C(31—35) of 7.6(4)°). The amide planes are oriented so that their NH groups point to the same face of the cyclohexane ring. The dihedral angle subtended by the amide planes {C21, N1, O1} and {C41, N2, O2} is 79.6(5)°.

Adjacent molecules related by the crystallographic 2_1 screw axes are interconnected *via* pairs of N—H···O hydrogen bonds into infinite columnar stacks oriented in the direction of the crystallographic *b* axis (see Figure) [14]. These interactions are supported by the relatively weaker C—H···O interactions between the ferrocene CH groups adjacent to the amide NH (C15 and C35) as the donors and the amide C=O moieties as the acceptors. The hydrogen bond parameters are as follows: N1—H1N···$O2^i$: N1···$O2^i$ = 3.008(4) Å, angle at H1N = 155°; N2—H2N···$O1^i$: N2···$O1^i$ = 2.947(4) Å, angle at H2N = 154°; C15—H15···$O2^i$: C15···$O2^i$ = 3.325(5) Å, angle at H15 = 158°; and C35—H35···$O1^i$: C35···$O1^i$ = 3.304(5) Å, angle at H35 = 138°; where $i = 1 - x, -1/2 + y, 1 - z$.

Acknowledgements: Research leading to the presented results received support from the Czech Science Foundation (project no. 13-08890S). The authors are grateful to Dr. Ivana Císařová from the Department of Inorganic Chemistry, Faculty of Science, Charles University for collecting the diffraction data.

References

1. Kraatz, H.-B.; Lusztyk, J.; Enright, G. E.: Ferrocenoyl amino acids: a synthetic and structural study. Inorg. Chem. **36** (1997) 2400–2405.
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Crystallogr. **C71** (2015) 3–8.
4. Spek, A. L.: Structure validation in chemical crystallography. Acta Crystallogr. **D65** (2009) 148–155.
5. SAINT, version 8.34A. Bruker AXS Inc., Madison, WI, USA (2013).
6. SADABS, version 2014/4. Bruker AXS Inc., Madison, WI, USA (2014).
7. Parsons, S.; Flack, H. D.; Wagner, T.: Use of intensity quotients and differences in absolute structure refinement. Acta Crystallogr. **B69** (2013) 249–259.
8. Štěpnička, P.: Phosphinocarboxamides: the inconspicuous gems. Chem. Soc. Rev. **41** (2012) 4273–4305.
9. You, S.-L.; Hou, X.-L.; Dai, L.-X.; Cao, B.-X.; Sun, J.: Novel bis-*N*-[2-(diphenylphosphino)ferrocenylcarbonyl] diaminocyclohexane ligands: application in asymmetric allylic alkylation of imino esters with simple allyl carbonate. Chem. Commun. (2000) 1933–1934.
10. Longmire, J. M.; Zhang, X.: Highly efficient kinetic resolution of 2-cyclohexenyl acetate in Pd-catalyzed allylic alkylation. Tetrahedron Lett. **41** (2000) 5435–5439.

11. El-Faham, A.; Albericio, F.: Peptide coupling reagents, more than a letter soup. Chem. Rev. **111** (2011) 6557–6602.
12. Cremer, D.; Pople, J. A.: General definition of ring puckering coordinates. J. Am. Chem. Soc. **97** (1975) 1354–1358.
13. Hanessian, S.; Gomtsyan, A.; Simard, M.; Roelens, S.: Molecular recognition and self-assembly by "weak" hydrogen bonding: Unprecedented supramolecular helicate structures from diamine/diol motifs. J. Am. Chem. Soc. **116** (1994) 4495–4496.
14. Motherwell, W. D. S.; Shields, G. P.; Allen, F. H.: Graph-set and packing analysis of hydrogen-bonded networks in polyamide structures in the Cambridge structural database. Acta Crystallogr. **B56** (2000) 857–871.