$[PtCl_2(C_{22}H_{19}FeP)_2].2C_6H_6$

Table 2. *Comparison of trans-[Pt(Cl)₂(PR₃)₂] complexes (Å, °)*

PR_3	Pt—P	Pt—Cl	P—Pt—Cl
Pcy₃[a]	2.337 (2)	2.317 (2)	88.8 (1)
PEt₃[b]	2.298 (18)	2.294 (9)	87.30 (14)
P('Bu)₂(CHCH₂CH₂)[c]	2.373 (1)	2.301 (1)	90.16 (4)
P{N(Me)CH₂CH₂}₃N[d]	2.349 (4)	Not reported	
P(NMe₂)₃[d]	2.3312 (7)	Not reported	
PPh₂Fc[e]	2.318 (2)	2.301 (2)	87.56 (7)

Notes: (a) Del Pra & Zanotti (1980); (b) Messmer & Amma (1966); (c) Simms, Shang, Lu, Youngs & Ibers (1987); (d) Xi *et al.* (1990); (e) this study.

Due to decay as a result of loss of the benzene solvate, data collection was only performed to $2\theta = 115°$. Coating of the crystal to minimize decay made description of crystal faces impossible and hence no absorption corrections were performed. The collected data were corrected for intensity decay. Although μ has a high value, effective $\mu^* t$ is small and constant due to the small equant crystal used for the data collection.

Data collection: Syntex *P*-1 software. Cell refinement: Syntex *P*-1 software. Data reduction: *PROFIT* (Streltsov & Zavodnik, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *OR-TEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

References

Adeleke, J. A. & Liu, L. (1993). *Acta Cryst.* C49, 680–682.
Del Pra, A. & Zanotti G. (1980). *Inorg. Chim. Acta*, 39, 137–141.
Houlton, A., Roberts, R. M. G., Silver. J. & Drew, M. G. B. (1990). *J. Chem. Soc. Dalton Trans.* pp. 1543–1547.
Johnson, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Messmer, G. G. & Amma, E. L. (1966). *Inorg. Chem.* 5, 1775–1781.
Miller, T. M., Kazi, J. A. & Wrighton, M. S. (1989). *Inorg. Chem.* 28, 2347–2355.
Otto, S. & Roodt, A. (1996). *Acta Cryst.* C52, 1636–1638.
Otto, S., Roodt, A. & Leipoldt, J. G. (1995). *S. Afr. J. Chem.* 48, 114–119.
Roodt, A., Otto, S. & Leipoldt, J. G. (1995). *Acta Cryst.* C51, 1105–1106.
Sheldrick, G. M. (1990). *Acta Cryst.* A46, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Simms, B. L., Shang, M., Lu, J., Youngs, W. J. & Ibers, J. A. (1987). *Organometallics*, 6, 1118–1126.
Sollott, G. P., Mertwoy, H. E., Portnoy, S. & Snead, J. L. (1963). *J. Org. Chem.* 28, 1090–1092.
Streltsov, V. A. & Zavodnik, V. E. (1989). *Kristallographia*, 34, 1369–1375.
Xi, S. K., Schmidt, H., Lensink, C., Kim, S., Wintergrass, D., Daniels, L. M., Jacobson, R. A. & Verkade, J. G. (1990). *Inorg. Chem.* 29, 2214–2220.

endo and *exo* Isomers of Isodicyclopentadienyltrichlorotitanium†

Judith C. Gallucci,[a] Natasha Kozmina,[a] Leo A. Paquette,[a] Florence Zaegel,[b] Philippe Meunier[b] and Bernard Gautheron[b]

[a]*Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA, and* [b]*Laboratoire de Synthèse et d'Electrosynthèse Organométalliques, Associé au CNRS (UMR 5632), Université de Bourgogne, 21000 Dijon CEDEX, France. E-mail: gallucci.1@osu.edu*

Abstract

The diastereomeric *endo* and *exo* isomers of the title complex, $[TiCl_3(C_{10}H_{11})]$, have been synthesized by electrophilic attack of $TiCl_4$ on the *exo*- or *endo*-trimethylsilyl derivative of isodiCp (isodiCp = isodicyclopentadiene). This reaction proceeds with net inversion of configuration to give exclusively either the *endo*- or *exo*-(isodiCp)TiCl₃ compound. Although the two isomers have similar unit-cell constants, they crystallize in different space groups. The *endo* complex, (2), is in *Pbcm* with a crystallographic mirror plane, while the *exo* complex, (4), is in *Pca*2₁ with pseudo-mirror symmetry. Both molecules display a distorted tetrahedral geometry about the Ti atom. Each Ti atom is bonded in a η^5 manner to the Cp ring of the isodiCp ligand, with Ti—ring centroid distances of 2.031 (2) and 2.013 (2) Å for (2) and (4), respectively. A slight bending of the isodiCp ligand about the bond shared by the Cp ring and the norbornane fragment is observed in both structures. The determination of the absolute structure of (4) defines the directionality of the packing along the polar c axis.
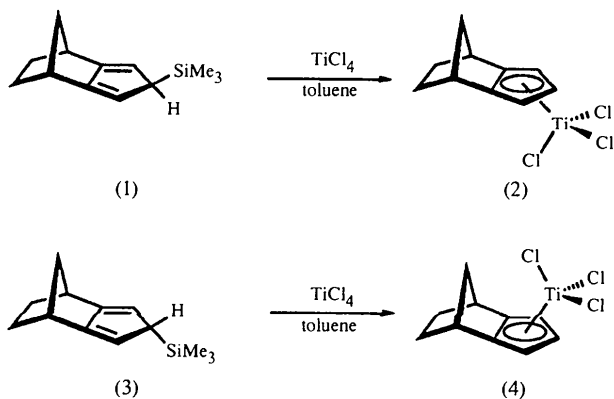
Comment

While the coordination of transition metals to C_2-symmetric annulated cyclopentadienyl anions necessarily gives rise to a single complex (Halterman, 1992), alternative recourse to C_1-symmetric 1,2-disubstituted cyclopentadienides allows for the possible production of pairs of π-facial isomers. This doubling of the number of possible products assumes practical utility when one face of the anion can be engaged in advance of the other by steric control (Paquette, Moriarty, McKinney & Rogers, 1989; Paquette, Moriarty & Rogers, 1989; Moriarty, Rogers & Paquette, 1989; Sivik, Rogers & Paquette, 1990; Rogers, Sivik & Paquette, 1993), by modulation of monomer–dimer equilibria in-

---

† Alternative name: trichloro[(1,2,3,3a,7a-η)-4,5,6,7-tetrahydro-4,7-methanoindenido]titanium.

volving Li counter ions (Paquette, Bauer *et al.*, 1990; Bauer, O'Doherty, Schleyer & Paquette, 1991; Bauer, Sivik, Friedrich, Schleyer & Paquette, 1992; Paquette, Sivik, Bauer & Schleyer, 1994) and/or by reaction temperature (Paquette, Moriarty, Meunier *et al.*, 1989; Sornay, Meunier, Gautheron, O'Doherty & Paquette, 1991).

We have previously demonstrated that very appreciable levels of control are attainable by one or more of the above techniques, as well as by prior silylation on the less hindered surface, followed by electrophilic attack with inversion of configuration (Paquette & Sivik, 1992). In this paper, comparison is made between ligand distortion, ligand orientation and metal environment in the diastereomeric *endo* and *exo* isomers, (2) and (4), respectively, of the title complex. For the preparation of (2), the *exo*-trimethylsilyl derivative (1) (Paquette, Charumilind, Kravetz, Böhm & Gleiter, 1983) was allowed to react with titanium tetrachloride in toluene over a temperature gradient of 195 K to room temperature. The high stereochemical control offered by this methodology is also seen in the response of *endo*-silane (3) (Paquette *et al.*, 1983), which gives rise uniquely to (4) under identical conditions.

upward toward the *c*-axis direction, which also prevents the molecule from containing a crystallographic mirror plane. As an example, the angle between the C1—C5 bond and the *c* axis is 10°. If the molecule had packed in the cell such that it contained a crystallographic mirror plane, this angle would be 0°. This slight skewing gives

Fig. 1. The molecular structure of (2) drawn with 50% probability displacement ellipsoids for the non-H atoms. The H atoms are represented by circles of artificial radii [symmetry code: (i) x, y, $\frac{1}{2} - z$].

The TiCl₃ group is bound in an *endo* fashion to the isodiCp (isodicyclopentadiene) ligand in (2) (Fig. 1) and in an *exo* manner in (4) (Fig. 2). The unit-cell dimensions for (2) and (4) are similar, but the molecules are not. While both molecules could contain a mirror plane, only (2) crystallized in *Pbcm* on a site with crystallographic mirror symmetry. Isomer (4) crystallized in the non-centrosymmetric *Pca*2₁ space group in such a manner that both the conformation of the molecule and its packing are slightly removed from mirror symmetry. The orientation of the TiCl₃ group is skewed slightly with respect to the isodiCp ligand so that mirror symmetry is broken. The torsion angle Cl1— Ti—ring centroid—C3 can be used as a measure of this skewing. It is 6.8 (2)° in this *exo* isomer. If exact mirror symmetry was present, this angle would be restricted to 0°. In the unit-cell drawing of (4) in Fig. 3, it is evident that the isodiCp ligands are oriented slightly
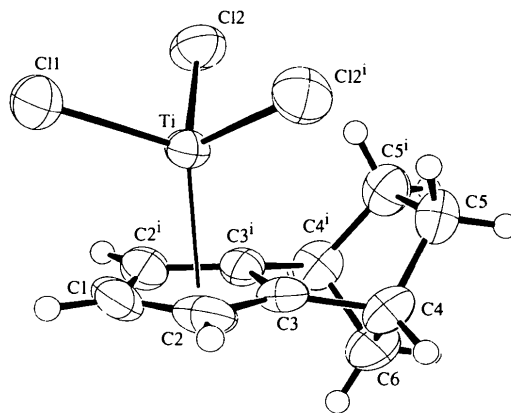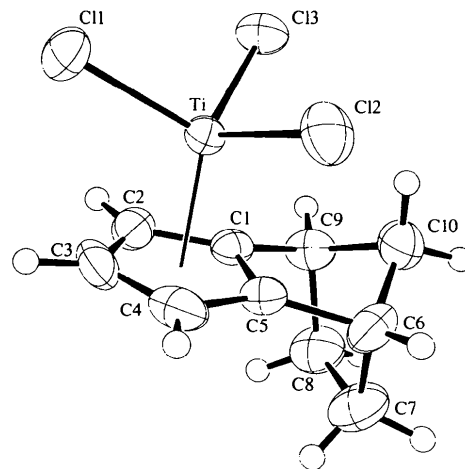
Fig. 2. The molecular structure of (4) drawn with 50% probability displacement ellipsoids for the non-H atoms. The H atoms are represented by circles of artificial radii.
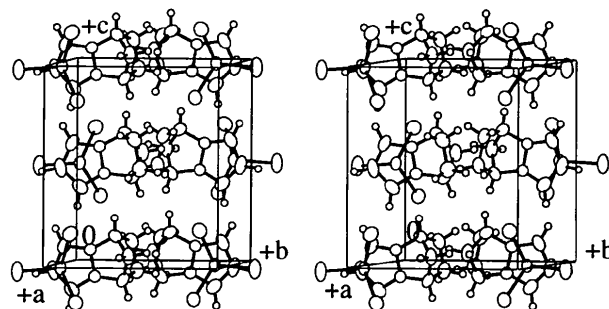

Fig. 3. Unit-cell drawing of (4) as viewed down the *a* axis.

the packing arrangement a directionality along the polar *c* axis. The determination of the absolute structure of (4) defines the directionality of this packing.

Both (2) and (4) display a distorted tetrahedral geometry about the Ti atom. The tetrahedron is defined by the three Cl atoms and the ring centroid of the approximately planar Cp ring of the isodiCp ligand. The Cl—Ti—Cl angles are slightly smaller than the tetrahedral value, while the Cl—Ti—ring centroid angles are slightly larger at 116.4(1) and 115.8(1)° in (2), and 113.2(1), 115.5(1) and 116.7(1)° in (4). Each Ti atom is bonded in a η^5 manner to a Cp ring, with the *endo* isomer showing a wider range of Ti—Cp ring C-atom distances than the *exo* isomer: 2.272(4)–2.424(2) Å for (2) *versus* 2.307(2)–2.365(2) Å for (4). The Ti—ring centroid distance is slightly longer in (2), at 2.031(2) Å, than in (4), at 2.013(2) Å.

It has been noted (Engelhardt, Papasergio, Raston & White, 1984) that in passing from CpTiCl$_3$ (Engelhardt *et al.*, 1984) to Cp$_2$TiCl$_2$ (Clearfield, Warner, Saldarriaga-Molina, Ropal & Bernal, 1975), the Ti—Cl bond lengths increase and the Cl—Ti—Cl angles decrease. This trend is also seen on comparison of (2) and (4) with (*exo*-isodiCp)$_2$TiCl$_2$ (Gallucci, Gautheron, Gugelchuk, Meunier & Paquette, 1987). In this latter structure, the Ti—Cl bond lengths are 2.366(1) and 2.356(1) Å, and the Cl—Ti—Cl angle is 92.94(2)°.

As observed in previous structures (Gallucci *et al.*, 1987), the isodiCp ligand in (2) and in (4) is bent slightly about the bond common to the Cp ring and the norbornane fragment [C3—C3^i in (2) and C1—C5 in (4); symmetry code: (i) $x, y, \frac{1}{2} - z$]. This bending moves the norbornane fragment in the direction away from the TiCl$_3$ group. As an example, in (4), the C6 and C9 atoms lie significantly out of the best least-squares plane through the five-membered ring of C1, C2, C3, C4 and C5, with the Ti atom lying on the opposite side of this plane. In (4), the bending can be described by the dihedral angle of 7.4(2)° between the best plane for atoms C1, C2, C3, C4 and C5, and the best plane for atoms C6, C5, C1 and C9. The analogous dihedral angle in (2) is 10.8(2)°. The observation that the *exo* isomer shows less bending than the *endo* isomer has also been seen in the diastereomers of (isodiCp)$_2$Ti(C$_6$F$_5$)Cl (Zaegel *et al.*, 1995). This is contrary to expectation, as the *exo* isomer should exhibit greater bending of the isodiCp ligand in the preferred *endo* direction (Paquette *et al.*, 1986; Paquette & Shen, 1990; Irngartinger, Deuter, Charumilind & Paquette, 1989).

Experimental

Stirring (1) (1.0 mmol) with TiCl$_4$ (1.0 mmol) in toluene for 1 h at 195 K and 10 h at room temperature gave (2) as red crystals with m.p. 387 K (from toluene) in 38% yield. Stirring

(3) (6.4 mmol) with TiCl$_4$ (6.4 mmol) in toluene for 1 h at 195 K and 2 h at room temperature gave (4) as red crystals with m.p. 461–464 K (from toluene) in 68% yield.

Compound (2)

Crystal data

[TiCl$_3$(C$_{10}$H$_{11}$)]	Mo $K\alpha$ radiation
$M_r = 285.46$	$\lambda = 0.7107$ Å
Orthorhombic	Cell parameters from 25
Pbcm	reflections
$a = 9.134(1)$ Å	$\theta = 14$–$15°$
$b = 12.328(1)$ Å	$\mu = 1.384$ mm^{-1}
$c = 10.314(1)$ Å	$T = 296$ K
$V = 1161.3(4)$ Å^3	Plate
$Z = 4$	$0.42 \times 0.23 \times 0.15$ mm
$D_x = 1.633$ Mg m^{-3}	Red
D_m not measured	

Data collection

Rigaku AFC-5S diffractometer	1080 reflections with $I > \sigma(I)$
ω–2θ scans	$R_{int} = 0.023$
Absorption correction:	$\theta_{max} = 27.5°$
ψ scan (North, Phillips & Mathews, 1968)	$h = -11 \rightarrow 11$
	$k = 0 \rightarrow 15$
$T_{min} = 0.735$, $T_{max} = 0.813$	$l = -13 \rightarrow 0$
3132 measured reflections	6 standard reflections
1414 independent reflections	every 150 reflections intensity decay: -0.2%

Refinement

Refinement on F	$\Delta\rho_{max} = 0.37$ e Å^{-3}
$R = 0.038$	$\Delta\rho_{min} = -0.33$ e Å^{-3}
$wR = 0.030$	Extinction correction: none
$S = 1.58$	Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV) (C, Cl, Ti) and Stewart, Davidson & Simpson (1965) (H)
1080 reflections	
70 parameters	
H atoms not refined	
Weighting scheme based on measured e.s.d.'s	
$(\Delta/\sigma)_{max} = 0.001$	

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

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

	x	y	z	U_{eq}
Ti	0.11770 (7)	0.02711 (5)	1/4	0.0403 (2)
Cl1	−0.1183 (1)	0.07537 (8)	1/4	0.0721 (4)
Cl2	0.19922 (8)	0.11900 (5)	0.07846 (7)	0.0602 (2)
C1	0.0314 (4)	−0.1457 (3)	1/4	0.068 (1)
C2	0.1197 (3)	−0.1374 (2)	0.3609 (3)	0.0576 (9)
C3	0.2646 (3)	−0.1263 (2)	0.3184 (2)	0.0417 (6)
C4	0.4223 (3)	−0.1355 (2)	0.3602 (3)	0.0526 (8)
C5	0.5077 (3)	−0.0323 (2)	0.3247 (2)	0.0539 (8)
C6	0.4748 (4)	−0.2121 (3)	1/4	0.065 (1)

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

Ti—Cl1	2.236 (1)	Ti—C2	2.329 (2)
Ti—Cl2	2.2288 (7)	Ti—C3	2.424 (2)
Ti—C1	2.272 (4)		
Cl1—Ti—Cl2	100.77 (3)	Cl2—Ti—Cl2^i	105.08 (4)

Symmetry code: (i) $x, y, \frac{1}{2} - z$.

C11—Ti—C12	103.59 (4)	C12—Ti—C13	103.91 (3)
C11—Ti—C13	102.21 (4)		

Compound (4)

Crystal data

[TiCl₃(C₁₀H₁₁)]
$M_r = 285.46$
Orthorhombic
$Pca2_1$
$a = 12.4368 (8)$ Å
$b = 9.062 (1)$ Å
$c = 10.3153 (9)$ Å
$V = 1162.6 (3)$ Å³
$Z = 4$
$D_x = 1.631$ Mg m⁻³
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 13–15°$
$\mu = 1.382$ mm⁻¹
$T = 296$ K
Rectangular rod
$0.35 \times 0.27 \times 0.19$ mm
Red

Data collection

Rigaku AFC-5S diffractometer
$\omega–2\theta$ scans
Absorption correction:
  analytical (De Meulenaer & Tompa, 1965)
$T_{min} = 0.680$, $T_{max} = 0.738$
4705 measured reflections
2675 independent reflections

2436 reflections with
$I > \sigma(I)$
$R_{int} = 0.013$
$\theta_{max} = 27.5°$
$h = -15 \rightarrow 16$
$k = 0 \rightarrow 11$
$l = -13 \rightarrow 13$
6 standard reflections
  every 150 reflections
  intensity decay: -5.3%

Refinement

Refinement on F
$R = 0.026$
$wR = 0.023$
$S = 1.70$
2436 reflections
126 parameters
H atoms not refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{max} = 0.009$
$\Delta\rho_{max} = 0.24$ e Å⁻³
$\Delta\rho_{min} = -0.20$ e Å⁻³

Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV) (C, Cl, Ti) and Stewart, Davidson & Simpson (1965) (H)
Absolute configuration: Flack (1983) x parameter, 1406 Friedel pairs

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (4)*

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

	x	y	z	U_{eq}
Ti	0.02295 (2)	0.10712 (4)	0	0.03564 (9)
C11	0.06519 (5)	−0.13241 (6)	−0.0156 (1)	0.0644 (2)
C12	0.11053 (7)	0.21008 (8)	−0.16631 (10)	0.0529 (2)
C13	0.11720 (7)	0.17754 (8)	0.17369 (10)	0.0541 (2)
C1	−0.1201 (2)	0.2465 (3)	0.0882 (3)	0.0337 (7)
C2	−0.1418 (3)	0.0949 (3)	0.1058 (3)	0.0474 (9)
C3	−0.1536 (2)	0.0321 (2)	−0.0180 (4)	0.0550 (8)
C4	−0.1390 (3)	0.1404 (4)	−0.1124 (3)	0.0500 (9)
C5	−0.1186 (2)	0.2736 (3)	−0.0452 (2)	0.0356 (6)
C6	−0.1091 (2)	0.4383 (3)	−0.0624 (3)	0.0501 (8)
C7	−0.2219 (2)	0.4957 (3)	−0.0180 (4)	0.0624 (9)
C8	−0.2246 (2)	0.4638 (3)	0.1276 (3)	0.0573 (9)
C9	−0.1134 (2)	0.3922 (3)	0.1547 (3)	0.0449 (7)
C10	−0.0424 (2)	0.4793 (3)	0.0581 (3)	0.0551 (8)

Table 4. *Selected geometric parameters (Å, °) for (4)*

Ti—C11	2.2391 (7)	Ti—C2	2.324 (3)
Ti—C12	2.2360 (9)	Ti—C3	2.307 (2)
Ti—C13	2.2341 (9)	Ti—C4	2.344 (3)
Ti—C1	2.364 (2)	Ti—C5	2.365 (2)

Because the intensity statistics appeared centrosymmetric for (2), the structure was solved in *Pbcm*. The Ti atom was located on a mirror plane by the Patterson method in *SHELXS86* (Sheldrick, 1990). Phasing on this atom in *DIRDIF* (Parthasarathi, Beurskens & Slot, 1983) revealed the remainder of the non-H atoms. Two octants of reciprocal space were measured and averaged together: $(h,k,-l)$ and $(-h,k,-l)$. A decay correction was unnecessary.

Three octants of reciprocal space were measured for (4): (h,k,l), $(-h,k,l)$ and $(h,k,-l)$. Because the intensity statistics appeared non-centrosymmetric, the structure was solved in $Pca2_1$. The Ti atom was found on a Patterson map and the rest of the atoms were located with standard structure-factor and Fourier calculations. Two of the octants of data were averaged together: (h,k,l) and $(-h,k,l)$. Most of the third octant $(h,k,-l)$ was treated as a unique set because of the anomalous scattering effect in this non-centrosymmetric space group. A linear decay correction was applied to the data (*TEXSAN*; Molecular Structure Corporation, 1989). The z coordinate of the Ti atom was fixed in order to define the origin along the polar c axis. The determination of the absolute structure was performed in *SHELXL93* (Sheldrick, 1993). The final *TEXSAN* model was refined along with the Flack x parameter in *SHELXL93* and a value of 0.03 (4) was obtained for this parameter (Flack, 1983). This indicates that the set of final *TEXSAN* coordinates is correct and it is this set which is reported here. As an additional test, the coordinates were inverted and then refined with the Flack x parameter and this resulted in a value of 0.97 (4) for x. H atoms for both structures are fixed at calculated positions with C—H = 0.98 Å and B(H) = 1.2B_{eq} (bonded C atom). *PLATON* was used to calculate some metric parameters (Spek, 1990).

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995) for (2); *TEXSAN* (Molecular Structure Corporation, 1989) for (4). Program(s) used to solve structures: *SHELXS86* for (2); *TEXSAN* (Molecular Structure Corporation, 1989) for (4). Program(s) used to refine structures: *TEXSAN* (Molecular Structure Corporation, 1995) for (2); *TEXSAN* (Molecular Structure Corporation, 1989) for (4). For both compounds, molecular graphics: *ORTEPII* (Johnson, 1976).

References

Bauer, W., O'Doherty, G. A., Schleyer, P. von R. & Paquette, L. A. (1991). *J. Am. Chem. Soc.* **113**, 7093–7100.

Bauer, W., Sivik, M. R., Friedrich, D., Schleyer, P. von R. & Paquette, L. A. (1992). *Organometallics*, **11**, 4178–4189.

Clearfield, A., Warner, D. K., Saldarriaga-Molina, C. H., Ropal, R., & Bernal, I. (1975). *Can. J. Chem.* **53**, 1622–1629.

Engelhardt, L. M., Papasergio, R. I., Raston, C. L. & White, A. H. (1984). *Organometallics*, **3**, 18–20.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Gallucci, J. C., Gautheron, B., Gugelchuk, M., Meunier, P. & Paquette, L. A. (1987). *Organometallics*, **6**, 15–19.

Halterman, R. L. (1992). *Chem. Rev.* **92**, 965–994.

Irngartinger, H., Deuter, J., Charumilind, P. & Paquette, L. A. (1989). *J. Am. Chem. Soc.* **111**, 9236–9237.

Johnson, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.

Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1992). *MSC/AFC Diffractometer Control Software.* Version 4.3.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1995). *TEXSAN. TEXRAY Structure Analysis Package.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Moriarty, K. J., Rogers, R. D. & Paquette, L. A. (1989). *Organometallics*, **8**, 1512–1517.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Paquette, L. A., Bauer, W., Sivik, M. R., Bühl, M., Feigel, M. & Schleyer, P. von R. (1990). *J. Am. Chem. Soc.* **112**, 8776–8789.

Paquette, L. A., Charumilind, P., Kravetz, T. M., Böhm, M. C. & Gleiter, R. (1983). *J. Am. Chem. Soc.* **105**, 3126–3135.

Paquette, L. A., Künzer, H., Green, K. E., De Lucchi, O., Licini, G., Pasquato, L. & Valle, G. (1986). *J. Am. Chem. Soc.* **108**, 3453–3460.

Paquette, L. A., Moriarty, K. J., McKinney, J. A. & Rogers, R. D. (1989). *Organometallics*, **8**, 1707–1713.

Paquette, L. A., Moriarty, K. J., Meunier, P., Gautheron, B., Sornay, C., Rogers, R. D. & Rheingold, A. L. (1989). *Organometallics*, **8**, 2159–2167.

Paquette, L. A., Moriarty, K. J. & Rogers, R. D. (1989). *Organometallics*, **8**, 1506–1511.

Paquette, L. A. & Shen, C.-C. (1990). *J. Am. Chem. Soc.* **112**, 1159–1164.

Paquette, L. A. & Sivik, M. R. (1992). *Organometallics*, **11**, 3503–3505.

Paquette, L. A., Sivik, M. R., Bauer, W. & Schleyer, P. von R. (1994). *Organometallics*, **13**, 4919–4927.

Parthasarathi, V., Beurskens, P. T. & Slot, H. J. B. (1983). *Acta Cryst.* A**39**, 860–864.

Rogers, R. D., Sivik, M. R. & Paquette, L. A. (1993). *J. Organomet. Chem.* **450**, 125–135.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Sivik, M. R., Rogers, R. D. & Paquette, L. A. (1990). *J. Organomet. Chem.* **397**, 177–185.

Sornay, C., Meunier, P., Gautheron, B., O'Doherty, G. A. & Paquette, L. A. (1991). *Organometallics*, **10**, 2082–2083.

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Zaegel, F., Gallucci, J. C., Meunier, P., Gautheron, B., Bzowej, E. I. & Paquette, L. A. (1995). *Organometallics*, **14**, 4576–4584.

Bis(nicotinamide-N)bis(salicylato-O,O')-copper(II), the Monoclinic Form

Ivan Leban,[a] Bojan Kozlevčar,[a] Joachim Sieler[b] and Primož Šegedin[a]

[a]*Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, PO Box 537, SLO-1001 Ljubljana, Slovenia, and* [b]*Institut für Anorganische Chemie, Universität Leipzig, Linnéstraße 3, D-04103 Leizpig, Germany. E-mail: ivan.leban@uni-lj.si*

Abstract

The monoclinic form of the title compound, [Cu(C₇H₅-O₃)₂(C₆H₆N₂O)₂], was isolated during the systematic synthesis of copper salicylates. A distorted octahedral coordination around Cu^{II}, located on the centre of symmetry, is formed by four carboxylic O atoms from two salicylate ligands [Cu—O 1.928 (2) and 2.766 (2) Å] and by two N atoms from two nicotinamide groups [Cu—N 2.022 (2) Å]. Monomeric structural units are linked together *via* hydrogen bonds of the type N—H···O between the N and O atoms of the nicotinamide ligands.

Comment

The crystal structure of the orthorhombic form of the title compound, (I), [Cu(sal)₂(nia)₂] (where sal is salicylate, $C_7H_5O_3^-$, and nia is nicotinamide, $C_6H_6N_2O$), along with a survey of similar complexes have been reported previously by Hoang, Valach & Melnik (1993). The orthorhombic compound crystallizes in space group *Pbca* (No. 61) with four stoichiometric C₂₆H₂₂CuN₄O₈ moieties in the unit cell. The orthorhombic form was prepared from Cu(sal)₂.4H₂O and nicotinamide in methanol. The single crystals were obtained on cooling the mixture to 268 K for 24 h. However, monoclinic crystals precipitate from a mixture of acetonitrile and methanol solution of the same starting components at room temperature. The monoclinic crystals have a distinctly different powder-diffraction pattern compared with the orthorhombic crystals.

(I)