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The Crystal Structures of *bis*-{(2-Benzotrifluoride)-[(2-oxo-3*H*-naphth-3-ylidene)-methyl]-aminato} Copper(II) and *bis*-{(3-Benzotrifluoride)-[(2-oxo-3*H*-naphth-3-ylidene)-methyl]-aminato} Copper(II)

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Summary. The *Schiff* base ligands 3-[(2-benzotrifluoride)-2-hydroxy-3*H*-naphth-3-ylidene)-methyl] aldamine (**1**) and 3-[(3-benzotrifluoride)-2-hydroxy-3*H*-naphth-3-ylidene)-methyl] aldamine (**2**) and their corresponding Cu(II) complexes (**I**, **II**) were synthesized. The crystal structures of *bis*-{(2-benzotrifluoride)-[(2-oxo-3*H*-naphth-3-ylidene)]-methyl]-aminato} Copper(II) (**I**) and *bis*-{(3-benzotrifluoride)-[(2-oxo-3*H*-naphth-3-ylidene)-methyl]-aminato} Copper(II) (**II**) were determined. Compound **I** crystallizes in the triclinic crystal system ($a = 12.561(3)$, $b = 16.211(4)$, $c = 8.007(2)$ Å, $\alpha = 96.29(2)$, $\beta = 101.42(2)$, $\gamma = 97.10(2)°$, space group $P_{\bar{1}}$, $Z = 2$); compound **II** crystallizes in the monoclinic crystal system ($a = 5.064(2)$, $b = 19.172(4)$, $c = 15.111(3)$ Å, $\beta = 95.05(2)°$, space group $P2_1/c$, $Z = 2$). The X-ray diffraction study shows that the geometry around the metal atom is square planar for both copper complexes.

Keywords. Hydroxy-naphthaleñic *Schiff* bases; *Schiff* base Copper(II) complexes; Crystal structure

Kristallstruktur von *bis*-{(2-Benzotrifluorid)-[(2-oxo-3*H*-naphth-3-yliden)-methyl]-aminato}-Kupfer(II) und *bis*-{(3-Benzotrifluorid)-[(2-oxo-3*H*-naphth-3-yliden)-methyl]-aminato}-Kupfer(II)

Zusammenfassung. Die *Schiff*schen Basen 3-[(2-Benzotrifluorid)-2-hydroxy-3*H*-naphth-3-yliden)-methyl]-aldamin (**1**) und 3-[(3-Benzotrifluorid)-2-hydroxy-3*H*-naphth-3-yliden)-methyl]-aldamin (**2**) sowie ihre entsprechenden Cu(II)-Komplexe (**I**, **II**) wurden synthetisiert und ihre Struktur im Kristall bestimmt. Verbindung **I** kristallisiert triklin ($a = 15.561(3)$, $b = 16.211(4)$, $c = 8.007(2)$ Å, $\alpha = 96.29(2)$, $\beta = 101.42(2)$, $\gamma = 97.10(2)°$, Raumgruppe $P_{\bar{1}}$, $Z = 2$); Verbindung **II** kristallisiert monoklin ($a = 5.064(2)$, $b = 19.172(4)$, $c = 15.111(3)$ Å, $\beta = 95.05(2)°$, Raumgruppe $P2_1/c$, $Z = 2$). Aus der Röntgenstrukturanalyse ergibt sich eine quadratisch planare Geometrie der Komplexe.

Introduction

Although metal *Schiff* base complexes derived from salicylaldehyde have been extensively studied [1–3], there are few X-ray structural studies of the 1,2- and 2,3-naphthalenic analogues [4–11]. In a previous paper [12] we described the

Table 1. Summary of crystal and intensity collection data for I and II

Compound	I	II
Formula	$C_{36}H_{22}N_2O_2F_6Cu$	$C_{36}H_{22}N_2O_2F_6Cu$
Molecular weight	692.104	692.104
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Crystal colour	Brown red	Brown red
T	298 K	298 K
Crystal dimensions (mm)	0.26 × 0.38 × 0.26	0.08 × 0.10 × 0.40
a(Å)	12.561(3)	0.064(2)
b(Å)	16.211(4)	19.172(4)
c(Å)	8.007(2)	15.111(3)
α(°)	96.29(2)	90
β(°)	101.42(2)	95.05(2)
γ(°)	97.10(2)	90
V(Å^3)	1580.31	1461.4(5)
h, k, l ranges	$-14 < h < 14$	$0 < h < 5$
	$-18 < k < 18$	$0 < k < 22$
	$0 < l < 8$	$-17 < l < 17$
$\rho_{calc.}$ (mg m^{-3})	1.454	1.573
Z	2	2
F(000)	702	702
μ(cm^{-1})	15.72	8.24
Unique reflections	3970	2551
Observed reflections	3629	1400
R	0.046	0.076
R_W	0.063	0.069

crystal and molecular structures of two *Schiff* base copper(II) complexes derived from 2-hydroxy-3-naphthaldehyde: *bis*-{(phenyl)-[(2-oxo-3*H*-naphth-3-ylidene)]-methyl]-aminato} copper(II) and *bis*-{(4-benzotrifluoride)-[(2-oxo-3*H*-naphth-3-ylidene)-methyl]-aminato} copper(II). In order to complete the series of copper(II) complexes with *Schiff* base bidentate ligands derived from 2-hydroxy-3-naphthaldehyde, where a benzotrifluoride radical is bonded to the imine nitrogen, we report in this paper the characterization of *bis*-{(2-benzotrifluoride)-[(2-oxo-3*H*-naphth-3-ylidene)-methyl]-aminato} copper(II) (**I**) and *bis*-{(3-benzotrifluoride)-[(2-oxo-3*H*-naphth-3-ylidene)-methyl]-aminato} copper(II) (**II**) as well as the single crystal X-ray analysis of **I** and **II**, in order to compare possible differences in stereochemistry resulting from the isomerism of the ligands and to see whether the influence of the CF_3 group modifies the geometry around the metal ion.

Results and Discussion

Some physical properties of the synthesized compounds are listed in Table 2. All compounds are soluble in dichloromethane or chloroform, but the complexes are less soluble than the ligands in other solvents such as alcohols, tetrahydrofuran,

Table 2. Color, melting points, molecular ions, magnetic moments, NMR and UV/Vis bands of the prepared compounds

Compound	Color	m.p. (°C)	M^+; [Base Peak] (m/e)	$\mu_{eff.}$ (B.M.)	NMR (ppm)	UV/Vis. (cm^{-1}) [ε]
1	Yellow	154–55	315; [315]	–	7.2–8.1 m (arom. H); 8.72 s (imine H); 12.08 s (OH)	25 641 [2 259] sh, 31 056 [26 966], 37 594 [38 581]
I	Brown-red	264–65	692; [315]	1.84	–	25 773 [4080] sh, 31 348 [45 481], 37 453 [67 025]
2	Yellow	155–57	315; [315]	–	7.25–8.0 m (arom. H); 8.81 s (imine H); 12.33 s (OH)	26 178 [2 148] sh, 30 960 [25 880] 37 736 [34 813]
II	Brown-red	>300	692; [115]	1.83	–	21 834 [3 177], 31 056 [45 960], 37 453 [90 568]

benzene, and ethyl acetate. The elemental analyses were satisfactory and demonstrated the complexes to have a ligand-to-metal ratio of 2:1. Mass spectra of the ligands show the expected molecular ion and the characteristic copper isotopic distribution. The NMR spectra for the ligands show signals characteristic of the naphthalene rings and the phenyl and benzene trifluoromethyl radicals. From two signals at low field one (*ca.* 12 ppm) disappears upon treatment with D_2O and can therefore be attributed to a phenolic proton, whereas the other one (*ca.* 8.8 ppm) is assigned to the proton bonded to the carbon atom of the imine group. A detailed study of the NMR spectra of the ligands will be published elsewhere [19].

Magnetic moments for complexes **I** and **II** are 1.84 and 1.83 B.M., respectively (Table 2) which is in agreement with the values described for this kind of compounds [20]. The infrared spectra of the ligands show the characteristic O–H absorption bands around 3400 cm^{-1} which disappear after complexation. The absorptions corresponding to C=N-vibrations are around 1640 cm^{-1} in the ligands; in the complexes they are splitted and shifted approximately 20 cm^{-1} to lower wave numbers as has been described for similar complexes [21, 22]. The electronic spectra of the complexes show only intraligand or charge transfer bands (see Table 2).

Final positional parameters for compounds **I** and **II** are given in Table 3 while, Table 4 contains a selection of bond lengths*. The structures of the complexes **I** and **II**, including atom-numbering schemes, are illustrated in Figs. 1 and 2, respectively. Although complexes **I** and **II** have similar structures, in **I** there are two crystallographic independent but structurally similar centrosymmetric molecules in the unit cell. In both **I** and **II**, the copper ion is four-coordinated and is bonded to the oxygen and nitrogen donor atoms of the two ligand molecules in a *trans* stepped

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* Additional material can be ordered from Fachinformationszentrum Karlsruhe, D-76344 Engenstein-Leopoldshafen, BRD (CSD-No. CSD-58182)

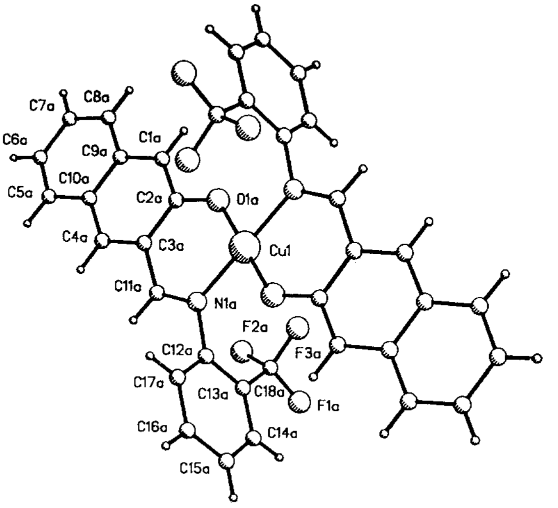

Fig. 1. Compound I

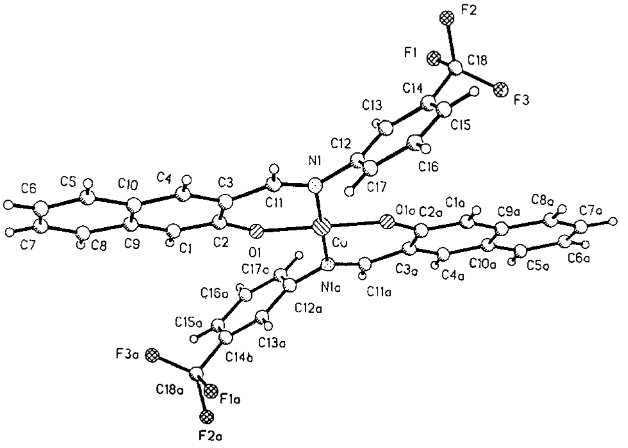

Fig. 2. Compound II

square planar structure, with a step for the two independent molecules of **I** (**Ia** and **Ib**) and for **II** of 0.80, 0.22 and 0.665 Å, respectively.

The Cu–O bond lengths in **I** are in the same range but slightly longer than the corresponding distances reported for *bis*-{(phenyl)-[(2-oxo-1*H*-naphth-1-ylidene)]-methyl]-aminato} copper(II) [7] and the two related *Schiff* base copper complexes derived from 2-hydroxy-3-naphthaldehyde, *bis*-{(phenyl)-[(2-oxo-3*H*-naphth-3-ylidene)]-methyl]-aminato} copper(II) and *bis*-{(4-benzotrifluoride)-[(2-oxo-3*H*-naphth-3-ylidene)-methyl]-aminato} copper(II) [12], while the Cu–N bond distances are similar. The same applies to the Cu–N and Cu–O bond lengths in **II** (2.045(6) and 1.852(6) Å, respectively). The C(11)–N(1) and N(1)–C(12) bond lengths (see Table 4) are in agreement with values found in related copper complexes [7, 12].

The trifluoromethyl groups in **II** show some amount of disorder which limited the precision of the structure determination at this site. Figure 1 shows only three of the eight observed fluorides. The closest approach between the nearest fluoride of the trifluoromethyl group to the copper atom in **I** (**Ia** and **Ib**) is 2.967 (F(3a)···Cu(1)) and 3.252 Å (F(1b)···Cu(2)), respectively.

Table 3. Atom coordinates (× 10^4) and isotropic displacement coefficients ($Å^2 \times 10^3$) for **I** and **II**

Atom	x	y	x	*U**
Compound I				
Cu(1)	0	0	0	46(1)
C(1a)	281(2)	−2055(2)	−3313(4)	51(1)
C(2a)	477(2)	−1500(2)	−1822(4)	48(1)
C(3a)	1128(2)	−1728(2)	−294(4)	50(1)
C(4a)	1517(3)	−2485(2)	−369(4)	56(1)
C(5a)	1740(3)	−3828(2)	−1987(5)	74(2)
C(6a)	1549(4)	−4337(2)	−35000(6)	82(2)
C(7a)	945(3)	−4116(2)	−4992(5)	76(2)
C(8a)	511(3)	−3377(2)	−4958(4)	61(1)
C(9a)	684(2)	−2822(2)	−3409(4)	51(1)
C(10a)	1313	−3046(2)	−1884(4)	56(1)
O(1a)	80(2)	−788(1)	−1832(3)	59(1)
C(11a)	1461(3)	−1167(2)	1290(4)	47(1)
N(1a)	1185(2)	−434(2)	1571(3)	47(1)
C(12a)	1669(2)	60(2)	3209(4)	43(1)
C(13a)	2439(3)	768(2)	3328(4)	51(1)
C(14a)	2833(3)	1260(2)	4889(5)	65(1)
C(15a)	2503(3)	1056(3)	6343(5)	70(1)
C(16a)	1748(3)	346(3)	6227(4)	64(1)
C(17a)	1331(3)	−145(2)	4668(4)	53(1)
C(18a)	2853(4)	995(3)	1784(5)	73(2)
F(1a)	3625(3)	1647(2)	2166(4)	123(1)
F(2a)	3243(2)	382(2)	1010(4)	112(1)
F(3a)	2061(2)	1184(2)	556(3)	109(1)
Cu(2)	5000	5000	0	49(1)
C(1b)	3658(3)	6518(2)	3265(5)	57(1)
C(2b)	4157(2)	6300(2)	1918(4)	49(1)
C(3b)	4674(3)	6958(2)	1163(4)	51(1)
C(4b)	4636(3)	7791(2)	1782(5)	62(1)
C(5b)	4218(3)	8868(2)	3898(6)	72(2)
C(6b)	3811(3)	9045(2)	5311(6)	75(2)
C(7b)	3321(3)	8404(2)	6060(6)	79(2)
C(8b)	3250(3)	7581(2)	5409(5)	68(1)
C(9b)	3685(2)	7363(2)	3941(4)	55(1)
C(10b)	4177(3)	8013(2)	3167(5)	57(1)
O(1b)	4173(2)	5506(1)	1410(3)	67(1)
C(11b)	5278(3)	6811(2)	−130(4)	54(1)
N(1b)	5537(2)	6103(2)	−691(3)	49(1)
C(12b)	6259(3)	6145(2)	−1896(4)	48(1)
C(13b)	7376(3)	6298(2)	−1333(4)	52(1)
C(14b)	8040(3)	6357(2)	−2558(5)	66(1)
C(15b)	7572(3)	6279(2)	−4272(4)	70(1)
C(16b)	6479(3)	6116(3)	−4785(5)	76(2)
C(17b)	5799(3)	6036(2)	−3615(5)	69(1)
C(18b)	7931(3)	6405(3)	505(5)	77(2)

(*Continued*)

Table 3. (*Continued*)

Atom	x	y	x	U*
F(1b)	7542(2)	5829(2)	1348(3)	112(1)
F(2b)	7754(3)	7103(2)	1365(4)	140(2)
F(3b)	8986(2)	6404(4)	777(4)	185(2)
Compound II				
Cu	5000	5000	5000	37(1)
O(1)	2330(11)	4543(3)	5530(4)	49(2)
N(1)	5058(13)	5805(3)	5889(4)	33(2)
C(1)	1311(16)	5258(4)	7711(5)	36(3)
C(2)	2296(15)	5201(3)	6893(5)	30(3)
C(3)	1373(16)	4640(4)	6306(6)	36(3)
C(4)	−524(17)	4207(4)	6582(6)	43(3)
C(5)	−3549(17)	3813(5)	7694(6)	46(3)
C(6)	−4462(19)	3887(5)	8498(6)	52(4)
C(7)	−3459(18)	4405(5)	9092(6)	48(3)
C(8)	−1596(19)	4863(4)	8845(6)	53(4)
C(9)	−563(17)	4809(4)	8009(5)	37(3)
C(10)	−1543(16)	4266(4)	7412(5)	36(3)
C(11)	4020(16)	5738(4)	6634(5)	35(3)
C(12)	6570(15)	6432(4)	5789(5)	29(3)
C(13)	6167(17)	6815(4)	5010(5)	41(3)
C(14)	7590(18)	7419(4)	4895(6)	41(3)
C(15)	9432(18)	7648(5)	5565(7)	50(4)
C(16)	9830(19)	7270(4)	6346(6)	49(3)
C(17)	8375(16)	6666(4)	6455(5)	40(3)
C(18)	7026(31)	7835(6)	4060(9)	74(6)
F(1)	4932(42)	7653(10)	3537(12)	52(8)°
F(2)	5646(50)	8442(10)	4232(11)	97(10)°
F(3)	9296(67)	7806(24)	3613(21)	96(15)°
F(4)	9056(43)	8292(11)	3943(11)	87(9)°
F(5)	8421(68)	7456(15)	3379(14)	62(12)°
F(6)	4476(57)	7951(18)	3861(20)	79(13)°
F(7)	7573(58)	8487(10)	4152(11)	64(10)°
F(8)	6638(82)	7529(10)	3370(13)	71(10)°

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

° Isotropic U, partial occupation

Bond lengths and bond angles in the naphthalene rings are very similar in both complexes and show some differences from naphthalene itself as expected for a chelate derivative [23]. Bond angles in complexes **I** and **II** show also that the coordination geometry around the copper atoms is square planar with O(1)–Cu–N(1) and O(1)–Cu–N(1a) angles of 91.7(1) and 88.3(1) (**Ia**), 90.8(1) and 89.2(1) (**Ib**), and 92.4(3) and 87.6(3)° (**II**), respectively. Other angles show expected values.

The mean planes through the naphthalene rings, the chelate rings, the coordination planes, and the benzene rings were calculated. In both complexes, we

Table 4. Selected bond lengths (Å) for **I** and **II**

Compound I		Compound II	
Cu(1)–O(1a)	1.915(2)	Cu–O(1)	1.862(6)
Cu(1)–N(1a)	1.978(2)	Cu–N(1)	2.045(3)
Cu(2)–O(1b)	1.896(3)	Cu–O(1a)	1.852(6)
Cu(2)–N(1b)	1.980(2)	Cu–N(1a)	2.045(3)
O(1a)–C(2a)	1.312(4)	O(1)–C(2)	1.320(11)
O(1b)–C(2b)	1.331(4)	C(2)–C(3)	1.446(11)
C(11a)–N(1a)	1.298(4)	N(1)–C(11)	1.290(10)
C(11b)–N(1b)	1.310(4)	N(1)–C(12)	1.440(10)
N(1a)–C(12a)	1.474(3)	N(1a)–C(12a)	1.441(4)
N(1b)–C(12b)	1.448(4)	C(3)–C(11)	1.427(11)
C(2a)–C(3a)	1.426(4)		
C(2b)–C(3b)	1.409(4)		
C(3a)–C(11a)	1.475(4)		
C(3b)–C(11b)	1.426(5)		

can observe that the naphthalene and chelate ring planes of each ligand are nearly coplanar while the benzene-2-trifluoromethyl (**Ia** and **Ib**) and benzene-3-trifluoromethyl groups form an angle of 85.1, 69.3; 94.1, 98.1; and 60.0, 46.1° with the coordinating naphthaldimine groups respectively.

The X-ray data of all of the complexes involved in this study suggest that monosubstitution at the phenyl radical bonded to the imine nitrogen has no effect on the geometry ground the copper(II) ion.

Experimental

Melting points were determined in a Fisher–Jones melting point apparatus and are uncorrected; infrared spectra (KBr disks) were recorded on a Perkin–Elmer Mod. 203-B spectrometer, UV/Vis spectra on a Perkin-Elmer Mod 552 spectrophotometer using chloroform as solvent; mass spectra were obtained using a Hewlett–Packard instrument Mod. 5985 at 70 eV ionizing potential; NMR spectra were recorded on a Varian FT-80B spectrometer using $CDCl_3$ as solvent; magnetic moment measurements were made with a Johnson Matthey magnetic susceptibility balance at 24 °C. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee, USA.

The chemicals 2-aminobenzotrifluoride, 3-aminobenzotrifluoride, and Copper(II) acetate monohydrate were purchased from Aldrich and were used without further purification. 2-Hydroxy-3-naphthaldehyde was prepared as described in Ref. [13] using naphthol (Koch & Light Labs. Ltd.) as starting material. Ligands and copper complexes were prepared by methods described elsewhere [14, 15].

Crystals of **I** and **II** were grown by slow diffusion of MeOH into a CH_2Cl_2 solution. The X-ray data for the two compounds were collected on a Nicolet P3F four-circle diffractometer (**I**: Ni-filtered CuK_α radiation ($\lambda = 1.54178$ Å), lattice constants from setting angles of 25 strong reflections with $8.48 < 2\theta < 23.64°$, intensities by $\omega - 2\theta$ scan mode with variable scan speed; **II**: graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å), lattice constants from setting angles of 25 strong reflections with $10.34 < 2\theta < 24.97°$, intensities by $\omega - 2\theta$ scan mode with variable scan speed). Corrections were applied for *Lorentz* and polarization effects. Crystal data and additional data collection parameters are given in Table 1.

The structures were solved by direct methods and subsequent *Fourier* difference maps. They were refined by the full-matrix least-squares method using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed in idealized positions with a fixed isotropic temperature factor ($U = 0.06\,\text{Å}^2$) and included in the refinement.

The atomic scattering factors were taken from Ref. [16]. Solution and refinement of **I** was carried out by using the SHELXTL program [17] while **II** was evaluated by the SHELXTL-PLUS PC Version [18].

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