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# Crystal structures of *trans*-di(2-fluorobenzoato-O)di-(1,3-diaminopropane-N,N')nickel(II) and its copper(II) analogue. Variation in the coordination modes

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# Abstract

The structures of di(2-fluorobenzoato-*O*)di(1,3-diaminopropane-*N*,*N*<sup>\*</sup>)copper (II) (1) and *trans*-di(2-fluorobenzoato-*O*)bis(1,3-diaminopropane-*N*,*N*<sup>\*</sup>)nickel(II) (2) were determined by single-crystal X-ray methods. I: { $Cutn_2(2FbzO)_2$ } (tn = 1,3-diaminopropane, 2FbzO=*ortho*-fluorobenzoate),  $C_{20}H_{28}F_2CuN_4O_4$ ,  $M_i = 490.01$ , monoclinic, space group  $P2_3/n$  No. 14, a = 15.189(3), b = 8.446(4), c = 26.846(4) Å,  $\beta = 106.20(1)^\circ$ , V = 3307(2) Å<sup>3</sup>, Z = 6,  $D_c = 1.476 g cm^{-3}$ . 2; {Ni(tn)<sub>2</sub>(2FbzO)<sub>2</sub>},  $C_{29}H_{28}F_2NiN_4O_4$ ,  $M_i = 485.15$ , monoclinic, space group  $P2_1/a$  No. 14, a = 11.280(2), b = 8.423(2), c = 11.568(3) Å,  $\beta = 96.37(2)$ , V = 1092.3(9) Å<sup>3</sup>, Z = 2,  $D_c = 1.512 g cm^{-3}$ . In compounds 1 and 2 the chelate rings display a chair conformation and there is *trans* coordination around the central metal cation. In 1 there are two crystallographically independent complex units, which represent different modes of conformational isomerism. In the first one the central copper(II) ion sits at a centre of symmetry, whereas in the second the site symmetry is only  $C_1$ . In 2 the site symmetry around the central nickel(II) cation is  $C_c$ . All the axial M-O bond lengths exhibit axial elongation Extended Hückel calculations suggest that the nature of the axial bonding in the two compounds is essentially different. In the copper(II) complex units it is affected by d-s mixing, whereas in the nickel(II) analogue the amount of d-s mixing is almost negligible. The effect of axial bonding is seen also in the geometry of the carboxylate groups. The most noticeable changes occur in the O-C-O angle of the carboxylate group. The effect of *ortho* substitution upon the benzoic acid and benzoate anion was investigated at the HF/6-31 + + G(d) level of theory. The incum variations are seen in the torsion angle of the carboxylate group.

Keywords: Crystal structures; Nickel complexes; Copper complexes, Benzoate complexes, Dianune complexes

# 1. Introduction

The coordination mode in a series of  $Mtn_2(bzO)_2$  (where M is either Cu(H), Ni(H) or Co(HI); bzO is either unsubstituted or substituted benzoate anion; tn is 1,3-diaminopropane) has been a topic in a large number of structural studies carried out in our laboratories. The list for the abhreviations used for the compounds mentioned in this work is shown in Table 1. Usually the complex units display centrosymmetric trans-bis coordination mode with the two six-membered chelate rings in chair conformation and the two axial sites occupied by coordinated benzoate anions. There are interesting exceptions in the Cu(H) complexes, however. In CUDINI the coordination number is five, whereas in CUAQMI the coordination mode is 4 + 1 + 1'. A benzoate anion can avoid totally the coordination, as found for CUORNI. So far, all five Ni(II) complexes of our series have displayed the centrosymmetric *trans*-bis coordination mode with the benzoate anions coordinated via one oxygen or hy-

In a historical note, the concept of 'semi-coordination' was introduced by Brown et al. to describe a long axial distance between a copper(II) ion and a weakly coordinated anion. The coordination was said to produce slight distortions in a coordinated anion, but clear enough to be detected by IR spectroscopy [15]. Quantum chemical studies of the electronic properties in bettzoate anions are scanty [5,16,17]. As far as we know, the effect of *ortho* substitution has been studied only once [18].

It has been suggested that octahedral (or pseudo-octahedral) Ni(II) complexes would exhibit a remarkable structural resemblance to the copper complexes [19]. Axial elongation in *trans*-MN<sub>4</sub>X<sub>2</sub>-type complexes (where M is either Cu(II) or Ni(II); X is a halogen) was mentioned as an example. To

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Table 1 Listing of the abbrev	iations for the compounds studied with their respective references
NIORFL	trans-di(2-fluorobenzoato-O)bis(1.3-diaminopropane-N,N')nicke

NIORFL	trans-di(2-fluorobenzoato-O)bis(1.3-diaminopropane-N,N')nickel(II)	this work
NIORME	trans-di(2-methylbenzoato-O)bis(1,3-diaminopropane-N,N')copper(11)	[1]
COPACL	trans-di(4-benzoato-O)bis(1,3-diaminopropane-N,N')cobalt(III) 4-chlorobenzoate	[2]
CUAOMI	aqua-di(1,3-diaminopropane-N,N')-3-iodobenzoatocopper(11) 3-iodobenzoate	[3]
CUBENZ	trans-di(benzoato-O)bis(1,3-diaminopropane-N,N')copper(II)	[4]
CUDINI	di(1,3-diaminopropane-N,N')-3,5-dinitrobenzoatocopper(11) 3,5-dinitrobenzoate	[5]
CUMEIO	trans-di(3-iodobenzoato-O)bis(1,3-diaminopropane-N,N')copper(II)	[6]
CUMENI	trans-di(3-nitrobenzoato-O)bis(1,3-diaminopropane-N,N') copper(II)	[7]
CUORFL	di(2-fluorobenzoato-O)di(1,3-diaminopropane-N,N')copper(II)	this work
CUORME	trans-di(2-methylbenzoato-O)bis(1,3-diaminopropane-N,N')copper(II)	[8]
CUORNI	trans-diaquabis(1,3-diaminopropane-NN)copper(II) di(2-nitrobenzoate)	[9]
CUTOSY	trans-di(4-methylbenzenesulfonato-O)bis(1,3-diaminopropane)copper(11)	[10]
NIMENI	trans-di(3-nitrobenzoato-O)bis(1,3-diaminopropane-N,N")nickel(II)	[11]
NIPAME	trans-di(4-methylbenzoato-O)bis(1,3-diaminopropane-N,N')nickel(II)	[12]
NIMEME	trans-di(3-methylbenzoato-O)bis(1,3-diaminopropane- $N,N'$ )nickel(11)	[13]
NIPANI	trans-di(4-nitrobenzoato-O)bis(1.3-diaminopropane-N,N')nickel(II)	[14]

explain this, d-s mixing was presented as a rationale for the similarities. As a result, the molecular orbital arising planarily from the  $3d_{2}$  orbital of Cu(II) or Ni(II) would have the lowest energy among the molecular orbitals arising from the d orbitals [19].

In our earlier report we suggested that the base strength of the 2-nitrobenzoate anion may be a reason for the exceptional coordination mode of CUORNI, where the water molecules occupy the axial sites instead of the 2-nitrobenzoate anions [9]. To study further the possible effect of *ortho* substitution on the coordination mode, we decided to use 2-fluorobenzoate as a counter anion. Also the dissociation constant and accordingly the base strength should be close to the values found for 2-nitrobenzoic acid. Moreover, structural information regarding either the 2-fluorobenzoic acid or its anion is very scarce [20.21].

The C-F···Fe<sup>2+</sup> interaction has been proposed as a cause of the extreme toxicity of fluorocitrate. Moreover, significant agostic F····M interactions are suggested to facilitate the formation of metal fluorides in {Ca(hfa)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub> and [Ba(hfa)<sub>2</sub>(H<sub>2</sub>O)]<sub>x</sub> (hfa = hexafluoroacetylacetone) [22]. As *ortho*-hydroxybenzoic acid forms a complex with tn and Cu<sup>2+</sup>, where the deprotonated hydroxy group is coordinated [23], we decided to investigate the coordination behaviour of *ortho*-fluorobenzoic acid.

We have prepared *trans*-di(2-fluorobenzoato-O)di(1,3diaminopropane-N,N')nickel(II) and its copper(II) analogue. A different synthesis route and the electronic spectrum of the Cu(II) compound wore published earlier by Melník [24]. We report here also the molecular structures of the two compounds determined by single-crystal X-ray methods. EHMO (extended Hückel molecular orbital) calculations were carried out for the complex units to evaluate the amount of d-s mixing. Moreover, the effects of *ortho* substitution and coordination on the benzoate anion were investigated by ab initio calculations at the HF/6-31 + + G(d) level of theory.

# 2. Experimental

# 2.1. Syntheses

CUORFL 2.90 mmol of 1,3-diaminopropane (Fluka) in 5 ml of MeCN were added to a solution of 1.40 mmol Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (Merck, p.a.), 3.00 mmol 2-fluorobenzoic acid (Sigma) and 3.00 mmol of triethylamine (Merck) in 33 ml of MeCN. The violet precipitate appeared immediately. The solution was allowed to stand at room temperature for 1.5 h. The raw product was filtered and washed with diethyl ether and acetone. The yield of the product was 65%. Recrystallisation was carried out by dissolving 101 mg of the raw product in 5 ml of absolute EtOH and 3 ml of diethyl ether. The solution was kept in a freezer (-18 °C) for 3 days. The deep blue crystals formed (70 mg) were filtered and washed with diethyl ether and acetone. Anal. Calc. for C<sub>20</sub>H<sub>28</sub>F<sub>2</sub>CuN<sub>4</sub>O<sub>4</sub>: Cu, 13.0; C, 49.02; N 11.43; H 5.76. Found Cu, 13.1; C, 48.82; N, 11.42; H, 5.80%.

*NIORFL*. A batch of 20 mmol NiCO<sub>3</sub> was dispersed into a solution containing 50 ml H<sub>2</sub>O and 100 ml EtOH. To this solution was added 40 mmol 2-fluorobenzoic acid (Sigma) and the mixture was stirred and boiled until there was a homogenous light green precipitate. Then 40 mmol 1,3-diaminopropane were added resulting in a light blue solution. Light blue crystals were separated upon cooling (1.930 g, yield 39.8%). Suitable single crystals for the subsequent Xray analysis were obtained by crystallising the raw product from MeOH. Anal. Calc. for  $C_{20}H_{28}F_2NiN_4O_4$ : C, 49.51; N 11.55; H 5.82. Found: C, 49.39; N, 11.42; H, 5.96%.

## 2.2. X-ray structure determination

### 2.2.1. Crystal data

*CUORFL*: [Cutn<sub>2</sub>(2FbzO)<sub>2</sub>], C<sub>20</sub>H<sub>28</sub>F<sub>2</sub>CuN<sub>4</sub>O<sub>4</sub>,  $M_r = 490.01$ , monoclinic, space group  $P2_1/n$  No. 14. a = 15.189(3), b = 8.446(4), c = 26.846(4) Å,  $\beta = 106.20(1)^{\circ}$ , V = 3307(2) Å<sup>3</sup> (by least-squares refinement of diffracto-

meter angles for 25 independent well-centred reflections measured in the 2 $\theta$  range of 29.2–37.5°,  $\lambda = 0.71069$  Å), F(000) = 1530, Z = 6,  $D_c = 1.476$  g cm<sup>-3</sup>. Dark blue plates. Crystal dimensions  $0.14 \times 0.20 \times 0.32$  mm,  $\mu = 10.40$  cm<sup>-1</sup>.

*NIORFL*: [Ni(tn)<sub>2</sub>(2FbzO)<sub>2</sub>], C<sub>20</sub>H<sub>28</sub>F<sub>2</sub>CuN<sub>4</sub>O<sub>4</sub>,  $M_r$  = 485.15, monoclinic, space group  $P2_1/a$  No. 14, a = 11.280(2), b = 8.423(2), c = 11.568(3) Å,  $\beta$  = 96.37(2), V = 1092.3(9) Å<sup>3</sup> (by least-squares refinement of diffractometer angles for 25 independent well-centred reflections in 2 $\theta$  range 23.2–37.1°,  $\lambda$  = 0.71069 Å), Z=2,  $D_c$  = 1.512 g cm<sup>-3</sup>, F(000) = 532, light blue plates. Crystal dimensions 0.21 × 0.28 × 0.35 mm,  $\mu$  = 9.42 cm<sup>-1</sup>.

### 2.2.2. Data collection and processing

CUORFL: Rigaku AFC5S diffractometer,  $\omega - 2\theta$  scan mode, scan speed 4.0° min<sup>-1</sup>, weak reflections with  $I < 10.0\sigma(I)$  twice rescanned, graphite monochromated Mo K $\alpha$  radiation, 8105 unique reflections measured ( $6 \le 2\theta \le 55^{\circ}$ ), giving 3556 observed reflections with  $I > 3\sigma(I_{o})$ . Neither decay nor absorption correction, but Lorentz and polarisation corrections were made.

*NIORFL*: Nicolet P3 diffractometer,  $\omega - 2\theta$  scan mode, variable scan speed 2.0–20.0° min<sup>-1</sup>, graphite monochromated Mo K $\alpha$  radiation, 3519 unique reflections measured ( $5 \le 2\theta \le 60^\circ$ ), no absorption correction, giving 2686 independent reflections with  $F > 5\sigma(F_o)$ . No decay, but Lorentz and polarisation corrections were made.

## 2.2.3. Structure analysis and refinement

CUORFL. The structure was solved by direct methods and refined by full-matrix least-squares techniques to an R value of 0.047 ( $R_w = 0.051$ :  $w = 1/[\sigma^2(F_o)]$ ). The heavy atoms were refined anisotropically, and the hydrogen atoms with fixed isotropic temperature factors (1.2 times  $B_{eq}$  of the carrying atom). Neutral atomic scattering and dispersion factors were taken from International Tables for X-Ray Crystallography [25]. All calculations were performed using the TEXSAN crystallographic software [26]. Figures were drawn with ORTEP [27].

NIORFL. Direct methods followed by difference Fourier techniques. Full-matrix least-squares refinement with all nonhydrogen atoms anisotropic and the hydrogens with isotropic temperature parameters. Final R and R' values are 0.037 and 0.043, respectively. The neutral atom scattering factors and correction factors for anomalous scattering were those included in the program package. The calculations were carried out with XTAL software [28]. The neutral atom scattering factors and correction factors for anomalous scattering were those included in the program package.

# 2.2.4. Quantum chemical calculations

These were carried out by the Gaussian 92 program package with 6-31 + + G(d) as the basis set [29]. The calculations were run on a CRAY X-MP computer of the Computer Centre of the Finnish State. The extended Hückel calculations were carried out by CACAO [30].

## 2.2.5. UV-Vis-NIR spectra

The solid state spectra were measured in Nujol mulls on a Cary 5E UV-Vis-NIR spectrometer. NIORFL displayed maxima at 350 (sh), 565, 806 and 1070 nm and CUORFL at 559 nm.

## 3. Results and discussion

## 3.1. General description of the compounds

The coordinates and selected bonds and angles are given in Tables 2 and 3, respectively. The complex units for the two compounds with the labelling scheme are shown in Figs. 1 and 2. Both compounds have similar overall structures. However, in CUORFL there are two independent complex units, which are named as unit I and II hereafter. The coordination polyhedra are elongated p-cudo-octahedra with two th ligands coordinated end central metal cation. The axial sites are occupied by two 2-fluorobenzoate anions. In NIORFL the coordination arrangement is more similar to that in the unit II, but the symmetry of the coordination polyhedron is quite near to octahe that. No direct agostic  $C-F\cdots M$ contacts are found.

In the complex unit  $f \circ f \cap UORFL$  there is no symmetry element involved and thus if  $\circ$  site symmetry around the central copper(II) atom is only  $C_1$  (Fig. 1). The coordination mode is clearly  $4 \div 1 \pm 1$ . The complex unit is the unique example of such as commetry in the series given in Table 1.

The most previous of breakdown of the symmetry is seen in the axial direction. The axial bond lengths Cu–O are highly significantly non-equal. The shorter distance Cu(1)–O(1) is only 2.345(3) Å, which is clearly shorter than the shortest found (2.468(3) Å for CUBENZ) in the series studied so far. However, it is still longer than 2.250(3) Å found in the five-coordinated CUDINI. The longer Cu(1)–O(3) bond length is 2.704(4) Å, which is longer than 2.665(2) Å (the longest axial bond found so far) in CUMENI.

In the complex unit II of CUORFL the central copper(II) cations sits in a centre of symmetry. Thus the site symmetry around Cu(II) is  $C_i$ . This is the usual coordination mode in our series. The axial bond length is 2.513(4) Å, which is similar to the value found for CUMEIO, 2.500(3). It is significantly longer than in CUBENZ, 2.468(3) Å, however.

Also in NIORFL the site symmetry around the central metal cation is  $C_i$  (Fig. 2). The axial bond length of 2.132(2) Å shows slight elongation, since the sum of the respective crystal ionic radii is 2.04 Å. All the other Ni(II) complexes in the series display similar elongation.

The six-membered chelate rings display chair conformation in the present compounds. Several descriptive values for the six-membered chelate rings in analogous compounds are shown in Table S1 (Section 4). In spite of the differences in the coordination mode of unit I, the puckering values for the two chelate rings look similar. The total puckering values Q[31] for the three chelate rings (0.658, 0.619 and 0.666 Å

Table 2 Positional parameters and  $B_{eq}$  for the non-hydrogen atoms in CUORFL, and atomic positional and isotropic displacement parameters for the non-hydrogen atoms in NIORFL

CUORFL	<i>x</i>	у	z	B <sub>eq</sub> <sup>2</sup>	
Cu(1)	0.83780(5)	0.47741(7)	0.17192(2)	2.47(3)	
Cu(2)	1/2	1/2	1/2	2.40(4)	
F(1)	1.1889(3)	0.6692(6)	0.1052(2)	7.2(2)	
F(2)	0.4973(3)	0.1578(5)	0.2020(2)	6.9(2)	
F(3)	0.1743(3)	0.2348(6)	0.5673(2)	6.6(2)	
O(1A)	1.0157(3)	0.5467(5)	0.1819(1)	3.7(2)	
O(1B)	0.6806(3)	0.4678(5)	0.1653(2)	3.6(2)	
0(1C)	0.3317(3)	0.4894(5)	0.4931(2)	3.9(2)	
O(2A)	1.0019(3)	0.6748(5)	0.1081(1)	3.8(2)	
O(2B)	0.6711(3)	0.2332(5)	0.2009(1)	3.9(2)	
O(2C)	0.3374(3)	0.2900(5)	0.5479(1)	3.6(2)	
N(1A)	0.8215(3)	0.5334(6)	0.0962(2)	2.7(2)	
N(1B)	0.8608(3)	0.4144(6)	0.2480(2)	3.0(2)	
N(1C)	0.5212(4)	0.4848(5)	0.5778(2)	2.7(2)	
N(2A)	0.8388(4)	0.7115(6)	0.1890(2)	3.2(2)	
N(2B)	0.8476(4)	0.2432(6)	0.1580(2)	3.1(2)	
N(2C)	0.5001(4)	0.2603(6)	0.4994(2)	2.8(2)	
C(1A)	0.7531(4)	0.6540(8)	0.0718(3)	3.7(3)	
C(1B)	0.9393(5)	0.3119(8)	0.2715(2)	3.8(3)	
C(1C)	0.6000(4)	0.3885(7)	0.6072(2)	3.1(2)	
C(2A)	0.7718(5)	0.8103(7)	0.1001(3)	3.9(3)	
C(2B)	0.9317(5)	0.1533(8)	0.2449(3)	4.1(3)	
C(2C)	0.5864(5)	0.2165(7)	0.5913(2)	3.3(3)	
C(3A)	0.7650(5)	0.8085(7)	0.1551(3)	3.7(3)	
C(3B)	0.9306(5)	0.1635(7)	0.1890(3)	3.5(3)	
C(3C)	0.5800(5)	0.1846(7)	0.5350(3)	3.3(3)	
C(4A)	1.1348(4)	0.7201(6)	0.1776(2)	2.8(2)	
C(4B)	0.5339(4)	0.3594(6)	0.1503(2)	2.5(2)	
C(4C)	0.1913(4)	0.3735(6)	0.4944(2)	2.6(2)	
C(5A)	1.1495(5)	0.7949(8)	0.2247(2)	4.9(3)	
C(5B)	0.4980(4)	0.4695(8)	0.1118(3)	4.2(3)	
C(5C)	0.1449(4)	0.4412(8)	0.4469(2)	4.1(3)	
C(6A)	1.2323(6)	0.873(1)	0.2471(3)	6.1(4)	
C(6B)	0.4050(5)	0.483(1)	0.0884(3)	5.8(4)	
C(6C)	0.0515(5)	0.429(1)	0.4256(3)	5.3(4)	
C(7A)	1.3009(5)	0.877(1)	0.2235(3)	5.5(4)	
C(7B)	0.3449(5)	0.3858(9)	0.1037(3)	4.7(3)	
C(7C)	0.0018(5)	0.351(1)	0.4529(3)	5.1(3)	
C(8A)	1.2868(5)	0.806(1)	0.1763(3)	5.3(4)	
C(8B)	0.3780(5)	0.2772(8)	0.1422(3)	4.3(3)	
C(8C)	0.0420(5)	0.2845(8)	0.5001(3)	4.8(3)	
C(9A)	1.2034(5)	0.7310(7)	0.1539(2)	3.8(3)	
C(9B)	0.4694(4)	0.2667(7)	0.1640(2)	3.6(3)	
C(9C)	0.1364(4)	0.2973(7)	0.5197(2)	3.5(3)	
C(10A)	1.0444(4)	0.0389(6)	0.1542(2)	2.6(2)	
C(10B) C(10C)	0.6370(4)	0.3514(7) 0.3856(7)	0.1744(2) 0.5133(2)	2.5(2)	
NIORFL	x/a	y/b	zlc	U <sub>eq</sub> <sup>b</sup>	
Ni(1)	1/2	1/2	0	0.0245(1)	
N(1)	0.6374(2)	0.5570(3)	-0.1019(2)	0.0340(6)	
N(2)	0.4603(2)	0.7437(3)	0.0018(2)	0.0360(6)	
0(1)	0.6197(1)	0.5273(2)	0.1548(1)	0.0353(5)	
O(2)	0.7273(2)	0.7399(2)	0.1186(1)	0.0483(6)	
C(1)	06118(2)	0.6677(4)	-0.1996(2)	0.0447(8)	
C(2)	0.5707(3)	0.8282(4)	-0.1605(3)	0.0498(9)	
C(3)	0.4522(2)	0.8292(3)	-0.1106(2)	0.0436(8)	
C(4)	0.7540(2)	0.6257(3)	0.3081(2)	0.0328(6)	
				(continued)	

Table 2 (continued	í	ì
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NIORFL	x/a	y/b	z/c	U <sub>eq</sub> <sup>b</sup>
C(5)	0.8651(2)	0.6853(3)	0.3449(2)	0.0462(8)
C(6)	0.9154(3)	0.6796(5)	0.4584(3)	0.065(1)
	0.8530(4)	0.6123(5)	0.5398(3)	0.072(1)
-18)	0.7429(4)	0.5520(5)	0.5075(3)	0.077(1)
C(9)	0.6934(3)	0.5559(4)	0.3931(2)	0.0540(9)
C(10)	0.6966(2)	0.6322(3)	0.1832(2)	0.0312(6)
F(1)	0.9328(2)	0.7493(3)	0.2680(2)	0.0952(9)

E.s.d.s are given in parentheses.

<sup>a</sup>  $B_{eq} = 1/3$  (trace of the orthogonalised  $B_{ij}$  matrix) for the non-hydrogen atoms.

<sup>b</sup>  $U_{eq} = 1/3$  (trace of the orthogonalised  $U_{ij}$  matrix) for the non-hydrogen atoms.

for the rings IA, IB and II, respectively) are comparable to those observed for the other Cu(II) compounds studied so far (0.597–0.662 Å). Also the values for NIORFL are similar to those found for the Cu(II) complexes. Generally, the chelate rings of the Cu(II) and Ni(II) compounds are more puckered than found for COPACL (0.510 and 0.585 Å). Obvicusly the unequality in the axial bonding in unit I in CUORFL results in differences in the puckering values of the rings, because the hydrogen bonding system is similar in both rings (Table S2, Section 4).

# 3.2. d-s mixing

The axial elongation in *trans*-CuL<sub>4</sub>L<sub>2</sub>' type complexes is usually explained by d-s mixing [19,32-34]. In their concluding remarks Vanquickenborne and co-workers [19] point out that, owing to the d-s mixing, the most stabilising distortion would be produced by an asymmetrical axial elongation. This would then lead either to five-coordination or the 4 + 1 + 1 coordination mode. However, most of the compounds in Table 1 display centrosymmetric structures. The only exceptions are CUDINI and CUAQMI with 4 + 1 and 4 + 1 + 1' coordination modes, respectively. To study the effect of d-s mixing, we performed extended Hückel calculations for each complex unit, since all the chromophores of this study are suitable for that purpose.

According to the results, the contribution of a 4s orbital in the two compounds is significantly different. In CUORFL the MO in the axial direction does have a significant contribution from the 4s orbitals, as predicted. The numerical values are 4 and 6% for the complex units I and II, respectively. However, in NIORFL the amount of d-s mixing is almost negligible (1%). In the copper(II) compounds shown in Table 1, the amount of d-s mixing varies in the range 5–8%, while for the nickel(II) compounds the value is  $\leq 1\%$ . The numerical values for the mixing are reasonable, however smaller than predicted by Vanquickenborne and co-workers [19]. The values obtained here are much smaller than obtained for planar copper(II) complexes (about 20%) [35–37].

Table 3
Selected bonding parameters for the two crystallographically independent complex units (numbering scheme in Fig. 1) in CUORFL (1) and NIORFL (2)

	CUORFL A	CUORFL B	CUORFL C	NIORFL	
M-N(1)	2.045(4)	2.033(4)	2.028(4)	2.104(2)	
M-N(2)	2.027(4)	2.029(5)	2.025(4)	2.102(2)	
MO(1)	2.345(3)	2.704(4)	2.513(4)	2.132(2)	
N(1)-M-N(2)	86.0(2)	89.5(2)	86.8(2)	87.35(9)	
O(1)-M-O(1)	169.39(14)	169.39(14)	180	180	
O(1A)-Cu(1)-N(1)	83.59(14)	94.01(14)			
O(1A)-Cu(1)-N(2)	79.8(2)	96.1(2)			
O(1B)-Cu(1)-N(1)	95.4(2)	87.3(2)			
O(1B)-Cu(1)-N(2)	89.7(2)	94.5(2)			
O(1C)-Cu(2)-N(1)			86.5(2)		
O(1C)-Cu(2)-N(2)			88.1(2)		
O(1)-Ni(1)-N(1)				90.47(7)	
O(1)-Ni(1)-N(2)				90.12(7)	



Fig. 1. ORTEP drawing showing the numbering scheme for the complex units I and II in CUORFL. The hydrogen atoms have been omitted for clarity. The thermal ellipsoids have been presented at the 50% probability level.

# 3.3. The geometry of the 2-fluorobenzoate anions

In each coordinated benzoate anion the fluorine atom lies at the same side of the aromatic ring with respect to the noncoordinated oxygen. Similar conformation is also found in CUORME and NIORME. However, in the *trans*-di-(*ortho*-aminobenzoato-O) bis(1,3-diaminopropane-N,N')copper(II) complex the *ortho* substituent lies on the same side of the ring as the coordinated oxygen [38].

Selected bond lengths and angles for the *ortho*-fluorobenzoate anions of the two compounds are listed in Table 4. In each observed fragment there are highly significant deviations from ideal geometry. The deformations take place especially in the angles in the vicinity of the fluorine substituent.



Fig. 2. ORTEP drawing showing the numbering scheme in NIORFL. The thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

The torsion angle of the carboxylate group around the C(4)-C(10) bond shows a wide variation. In 2-fluorobenzoic acid the angle is 10.6° [20] and in calcium 2-fluorobenzoate dihydrate it is 41° [21]. The torsion in an *ortho*-substituted benzoate anion is also pronounced in CUORME and NIORME, where the values are 61.0 and 64.5°, respectively. If the substituent is situated either at a *meta* or *para* position, the torsion angle is considerably smaller and ranges from 2.20 to 15.18° [2-7,11-14].

To study rurther the torsion angle, an MMX optimisation was performed for the 2-fluorobenzoate anion. The angle for

Table 4
Selected bonding parameters for ortho-fluorobenzoic acid (HORFL, optimised and observed [20]), its optimised anion (ORFL), NIORFL and CUORFL

anna agusan, yay Rostitika Utikin dalama na na di sakalangkan karanya Printeri da Siki anyaik	HORFLopt	HORFLobs	ORFL	NIORFL	CUORFL A	CUORFL B	CUORFL C
O(1)-C(10)	1.342	1.260(5)	1.261	1.256(3)	1.237(7)	1.247(8)	1.239(8)
O(2) - C(10)	1.217	1.223(5)	1.249	1.249(3)	1.263(6)	1.251(7)	1.262(6)
F(1)-C(5)	1.365	1.330(4)	1.374	1.347(4)	1.367(8)	1.351(7)	1.354(7)
C(4) - C(10)	1.475	1.463(6)	1.543	1.517(3)	1.506(8)	1.520(8)	1.522(8)
C(9)-C(4)-C(5)	117.43	117.5(4)	115.94	116.0(2)	116.6(5)	114.7(5)	115.0(5)
C(9)-C(4)-C(10)	116.68	120.0(4)	117.71	119.9(2)	119.2(6)	119.5(5)	119.3(5)
C(5)-C(4)-C(10)	125.90	122.5(4)	126.35	124.1(2)	124.1(5)	125.8(5)	125.7(5)
F(1) - C(5) - C(6)	116.29	117.5(4)	114.51	116.2(3)	118.1(7)	116.1(6)	116.8(6)
O(1)-C(10)-O(2)	121.11	123.0(4)	128.66	125.6(2)	124.8(5)	125.6(5)	125.3(5)
C(9)-C(4)-C(10)-O(1)	179.99	10.6(4)	- 4.99	-25.1(3)	-49.7(8)	14.7(8)	18.9(8)

the optimised structure is  $65.5^{\circ}$ . When the carboxylate group is rotated around the C(4)–C(10) bond by applying rigid rotor approximation, the maximum value during the rotation is 32.6 kJ mol<sup>-1</sup>. This is clearly a bigger value than 12 kJ mol<sup>-1</sup> found for the *para*-chlorobenzoate anion [2]. The maximum corresponds to a coplanar conformation. The range for an energy minimum window (where the energy is equal or less than 4 kJ mol<sup>-1</sup>) is rather wide, about 80°. Although the energy needed to rotate the carboxylate group was evaluated at the MMX level, the variation in the observed values supports the idea of almost free rotation in a wide range of rotation angles.

The geometry for *ortho*-fluorobenzoic acid and its corresponding anion was optimised by ab initio methods at the 6-31 + + G(d) level of theory, as well. Only the conformation similar to the coordinated anion (the fluorine atom *syn* to the hydroxyl group) was optimised for the acid form. Because the calculated IR spectra do not have any imaginary frequencies, the geometries are considered to represent the true minima. Selected bond lengths and angles for the optimised structures are given in Table 4.

The optimised acid molecule is practically coplanar having the torsion angle C(9)-C(4)-C(10)-O(1) of 179.99°. This planarity is in clear contrast with the result obtained by the semiempirical MMX methods mentioned above. The torsion angle for the optimised anion is also rather small,  $-4.99^{\circ}$ . There are considerable distortions from an ideal geometry, as seen in the angles in the vicinity of the fluorine substituent. Although the carboxylate group is almost coplanar in the optimised structure of the acid, it is bent away form the fluorine atom. This is seen in the angles C(5)-C(4)-C(10); the experimental values for the compounds studied here are in the range 124.1-125.8°. In a similar study carried out for 3,5-dinitrobenzoic acid and its anion in CUDINI the respective values were 120.3(4)-121.1(4)°. It seems that an inductive effect could play a role in the widening of the angle in the ortho-fluorobenzoates. Further studies are in progress to investigate the corresponding bromo and chloro analogues.

Also the bond C(4)-C(10) for the optimised anion is long, 1.553 Å. In the solid state the observed value for the acid is 1.463(6) Å [20]. The structure is dimeric with intradimeric hydrogen bonds, which are very likely to affect the electronic properties. The optimised structure of the acid is assumed to present a gaseous phase with no intermolecular contacts. In spite of this, the bond is rather short, 1.489 Å. The observed values in the present structures are quite near to the values of the optimised anion. A similar situation was found in CUDINI.

The C(10)–O(1) and C(10)–O(2) bond lengths do not have equal values. In the acid the C(10)–O(1) bond length is clearly longer than the C(10)–O(2) bond; in the complexes the situation tends to be reversed. Also in the anion form the bond lengths are different. This is in sharp contrast with the optimised values for 3,5-dinitrobenzoate and *para*chlorobenzoate anions, where the bond lengths are equal [5,2]. Obviously there must be an interaction between a fluorine substituent and a neighbouring oxygen. This would also explain the planarity of the optimised acid. No doubt, in the solid state hydrogen bonding affects the electronic distribution of a carboxylate group. The relevant hydrogen bonding parameters are given in Table S2 (Section 4). The intermolecular interactions between fluorine and oxygen.

The effect of complexation is seen especially in the O(1)-C(10)-O(2) angle, which shows a wide variation. The observed values for the angle in the complexes lie between the values obtained for the optimised acid and its anion. A similar behaviour was also found in CUDINI and COPACL.

## 4. Supplementary material

Listings for the descriptive parameters for the chelate rings (Table S1), hydrogen bonding parameters (Table S2) and a complete list for the atomic positional coordinates as well as the thermal motions are available from the authors on request.

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