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Syntheses and crystal structures of bis(4-dimethylaminopyridine) group 12 trifluoroacetates — $M(OCOCF_3)_2 \cdot 2DMAP$ ($M = Zn, Cd, Hg$)

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Dedicated to Professor Manfred Weidenbruch on the occasion of his 65th birthday

Abstract

Bis(4-dimethylaminopyridine) group 12 trifluoroacetates—$M(OCOCF_3)_2 \cdot 2DMAP$ ($M = Zn, Cd, Hg$) were prepared in quantitative yields from the anhydrous metal trifluoroacetates and DMAP. All compounds crystallize in the triclinic space group $P\bar{1}$ (no. 2) with two molecules per unit cell. While $Zn(OCOCF_3)_2 \cdot 2DMAP$ is built up by well-separated tetrahedral units exhibiting strongly covalent Zn–O bonds to monodentate trifluoroactate groups, $Cd(OCOCF_3)_2 \cdot 2DMAP$ and $Hg(OCOCF_3)_2 \cdot 2DMAP$ form dimeric units. The metal centers are distorted octahedrally surrounded by two axial DMAP ligands, two ionic bridging and one chelating trifluoroacetate group.

Keywords: Zinc; Cadmium; Mercury; Trifluoroacetate; Crystal structure

1. Introduction

Trifluoroacetates of group 12 elements are known for a long time and have been used for different synthetic purposes. However, the number of structurally characterized compounds is limited but even this small number exhibits structural diversity caused by different complex ligands.

Therefore, we started a systematic investigation on single crystal structures of groups 12 and 13 perhalocarboxylates mainly with the complex ligand DMAP. In this paper, a comparative investigation on the single crystal structures of $M(OCOCF_3)_2 \cdot 2DMAP$ ($M = Zn, Cd, Hg$; DMAP = 4-dimethylaminopyridine) is presented.

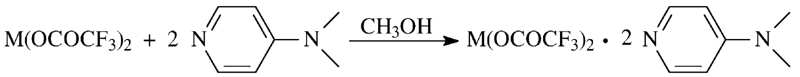
2. Results and discussion

2.1. Syntheses and characterizations of $M(OCOCF_3)_2 \cdot 2DMAP$ ($M = Zn, Cd, Hg$)

Anhydrous trifluoroacetates of main group 12 elements were prepared from the corresponding oxides and trifluoroacetic acid in the presence of trifluoroacetic acid anhydride to remove water produced in the course of the reaction [1] (Eq. (1)).

$$MO + 2CF_3COOH \xrightarrow{(CF_3CO)_2O} M(OCOCF_3)_2 + H_2O \qquad (1)$$

Complexes with DMAP are formed reacting $M(OCOCF_3)_2$ and two equivalents DMAP in boiling methanol (Eq. (2)).



(2)

Experimental details are given in Section 3.

All the derivatives had satisfactory elemental analyses. Decomposition points were determined to be 130 °C for $Zn(OCOCF_3)_2 \cdot 2DMAP$, 180 °C for $Cd(OCOCF_3)_2 \cdot 2DMAP$ and 216–220 °C for $Hg(OCOCF_3)_2 \cdot 2DMAP$.

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Table 1
Crystal data and structure refinement parameters for $Zn(OCOCF_3)_2 \cdot 2DMAP$ **I**, $Cd(OCOCF_3)_2 \cdot 2DMAP$ **II** and $[Hg(OCOCF_3)_2 \cdot 2DMAP] \cdot CH_3OH$ **III**

	I	**II**	**III**
Empirical formula	$C_{18}H_{20}F_6N_4O_4Zn$	$C_{18}H_{20}F_6N_4O_4Cd$	$C_{19}H_{24}F_6N_4O_5Hg$
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a (pm)	795.7(1)	1009.9(2)	1020.0(2)
b (pm)	898.6(2)	1028.4(2)	1027.3(3)
c (pm)	1606.9(3)	1213.0(2)	1178.1(2)
α (°)	79.80(1)	103.64(2)	95.84(2)
β (°)	81.43(1)	100.94(2)	103.96(1)
γ (°)	80.64(1)	106.22(2)	109.68(1)
Volume (nm^3)	1.1072(3)	1.1306(4)	1.1051(3)
Z	2	2	2
Formula mass ($g\ mol^{-1}$)	535.75	582.78	703.01
ρ_{calc} ($g\ cm^{-3}$)	1.607	1.712	2.113
μ (mm^{-1})	1.192	1.047	7.055
Absorption correction	Numerical	Numerical	Numerical
Transmission, maximum/minimum	0.6877/0.9242	0.7261/0.8938	0.2089/0.4560
θ Range (°)	2.33–26.00	1.80–26.00	1.82–27.20
Total data collected	13028	12055	12539
Index range	$-10 \le h \le 11$	$-12 \le h \le 13$	$-12 \le h \le 13$
	$-12 \le k \le 12$	$-12 \le k \le 13$	$-13 \le k \le 13$
	$-22 \le l \le 22$	$-15 \le l \le 15$	$-15 \le l \le 15$
Unique data	3961	4450	4761
Observed data	2872	2268	3461
Diffractometer	STOE Image Plate Diffraction System		
Radiation	Mo Kα (Graphite-Monochromator, $\lambda = 71.073$ pm)		
Temperature (K)	170(2)	170(2)	170(2)
R_{merg}	0.0813	0.1007	0.1045
R indexes [$I > 2\sigma I$]	$R_1 = 0.0417$	$R_1 = 0.0503$	$R_1 = 0.0589$
	$wR_2 = 0.0963$	$wR_2 = 0.1004$	$wR_2 = 0.1359$
R indexes (all data)	$R_1 = 0.0620$	$R_1 = 0.1187$	$R_1 = 0.0881$
	$wR_2 = 0.1042$	$wR_2 = 0.1237$	$wR_2 = 0.1442$
Goodness of fit (S_{obs})	1.069	0.875	1.136
Goodness of fit (S_{all})	0.961	0.736	1.016
No. of variables	379	379	319
$F(000)$	544	580	680
Largest difference map Hole/peak [$e\ 10^{-6}\ pm^{-3}$]	−0.424/0.501	−1.006/0.728	−1.986/1.875

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \left[\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^2)^2\right]^{1/2}$, $S_2 = \left[\sum w(|F_o|^2 - |F_c|^2)^2/(n-p)\right]^{1/2}$, with $w = 1/[\sigma^2(F_o)^2 + (0.0588P)^2]$ for $Zn(OCOCF_3)_2 \cdot 2DMAP$, $w = 1/[\sigma^2(F_o)^2 + (0.0600P)^2]$ for $Cd(OCOCF_3)_2 \cdot 2DMAP$ and $w = 1/[\sigma^2(F_o)^2 + (0.0669P)^2]$ for $[Hg(OCOCF_3)_2 \cdot 2DMAP] \cdot CH_3OH$ were $P = (F_o^2 + 2F_j^2)/3$. $F_c^* = kF_c[1 + 0.001|F_c|^2\lambda^3/\sin(2\theta)]^{-1/4}$.

2.2. Single crystal structure analyses

The nature of carboxylate coordination to metal centers can be: (i) monodentate; (ii) bridging; and (iii) chelating. Additionally, transitions between covalent and ionic bonding situations appear to be fluid. As a consequence different intermediate bonding modes have been formulated [2]. Crystallographic data are summarized in Table 1.

2.2.1. Bis(4-dimethylaminopyridine)zinc bis(trifluoroacetate), $Zn(OCOCF_3)_2 \cdot 2DMAP$

Although zinc bis(trifluoroacetate) is a commercially available compound, nothing is known about its structure and even the insight into complex derivatives is still limited. Five crystal structure analyses are reported [4–7] while further characterizations are missing (e.g. [8]) or are based mainly on vibrational spectra [9].

The crystal structure of $Zn(OCOCF_3)_2 \cdot 2DMAP$ is built up from well-separated tetrahedral units and is closely related to that of $Zn(OCOCH_3)_2 \cdot 2NC_5H_5$ [10]. The geometry around the zinc atom (Table 2, Fig. 1) is distorted tetrahedral; the central atom is coordinated by two oxygen atoms and two nitrogen atoms. Bond angles deviate up to approximately 12° from the regular tetrahedral angle.

Zinc–oxygen bond lengths are 198.5 and 197.9 pm and shorter than in further structures of zinc trifluoroacetate complexes [4–7] which are reported to be significantly longer than 200 pm. This might indicate a monodentate bonding mode with highly covalent character of the Zn–O bond in this complex compound. Secondary Zn–O contacts of 318.5 and 275.7 pm are out of range or very close to the sum of van der Waals radii which is calculated as 291 pm (139 pm for Zn, 152 pm for O) [11]. As a consequence of the monodentate coordination, carbon–oxygen bonds lengths

Table 2
Selected internuclear distances (pm) and angles (°) for the compounds $Zn(OCOCF_3)_2·2DMAP$, $Cd(OCOCF_3)_2·2DMAP$ and $[Hg(OCOCF_3)_2·2DMAP]·CH_3OH$

$Zn(OCOCF_3)_2·2DMAP$			
Zn–N 11	200.6(3)	N 11–Zn–N 21	116.9(1)
Zn–N 21	199.2(3)	N 11–Zn–O 311	97.2(1)
Zn–O 311	198.5(3)	N 11–Zn–O 411	110.7(1)
Zn–O 312	318.5(5)	N 21–Zn–O 311	106.7(1)
Zn–O 411	197.9(2)	N 21–Zn–O 411	115.6(1)
Zn–O 412	275.7(5)	O 311–Zn–O 411	107.7(1)
C 31–O 311	126.0(4)		
C 31–O 312	121.1(4)		
C 31–C 32	152.7(5)		
C 41–O 411	127.0(4)		
C 41–O 412	121.8(4)		
C 41–C 42	153.2(5)		
$Cd(OCOCF_3)_2·2DMAP$			
Cd–N 11	223.9(6)	N 11–Cd–N 21	171.1(2)
Cd–N 21	223.9(6)	N 11–Cd–O 311	93.8(2)
Cd–O 311	244.7(5)	N 11–Cd–O 312	92.0(2)
Cd–O 312	247.5(5)	N 11–Cd–O 411	85.1(2)
Cd–O 411	240.5(6)	N 11–Cd–O 412’	91.7(2)
Cd–O 412′	242.0(5	N 21–Cd–O 311	94.5(2)
Cd–Cd′	397.6(4)	N 21–Cd–O 312	90.5(2)
C 31–O 311	123.8(8)	N 21–Cd–O 411	86.3(2)
C 31–O 312	125.2(9)	N 21–Cd–O 412′	92.0(2)
C 31–C 32	151.8(9)	O 311–Cd–O 411	146.0(2)
C 41–O 411	123.1(9)	O 311–Cd–O 412′	85.0(2)
C 41–O 412	124.8(9)	O 311–Cd–O 312	53.9(2)
C 41–C 42	148.8(9)	O 411–Cd–O 412′	128.9(2)
		O 312–Cd–O 412′	138.9(2)
		O 312–Cd–O 411	92.2(2)
$[Hg(OCOCF_3)_2·2DMAP]·CH_3OH$			
Hg–N 11	205.4(9)	N 11–Hg–N 21	172.9(4)
Hg–N 21	204.0(9)	N 11–Hg–O 311	92.1(3)
Hg–O 311	262.7(9)	N 11–Hg–O 312	89.3(3)
Hg–O 312	280.0(9)	N 11–Hg–O 411′	92.2(3)
Hg–O 411′	269.5(9)	N 11–Hg–O 412	85.6(4)
Hg–O 412	282.0(9)	N 21–Hg–O 311	92.7(3)
Hg–Hg′	371.3(7)	N 21–Hg–O 312	90.0(3)
C 31–O 311	124.8(9)	N 21–Hg–O 411′	93.3(3)
C 31–O 312	123.0(9)	N 21–Hg–O 412	87.4(3)
C 31–C 32	154.0(9)	O 311–Hg–O 411′	86.1(3)
C 41–O 411	124.9(9)	O 311–Hg–O 412	127.2(4)
C 41–O 412	118.0(9)	O 311–Hg–O 312	48.3(3)
C 41–C 42	160.0(9)	O 312–Hg–O 412	79.0(3)
		O 412–Hg–O 411′	146.6(4)
		O 312–Hg–O 411′	134.4(4)

around C 31 and C 41 significantly differ from each other. While C–O bonds to the metal coordinated oxygen atoms are in the expected region of a C–O single bond (126.0 and 127.0 pm) those to the second oxygen atom are shorter (121.1 and 121.8 pm) indicating double bond character.

Zinc–nitrogen distances (199.2 and 200.6 pm) are in good agreement with those reported for the complexes $Zn(NCO)_2·2DMAP$ and $Zn(NCS)_2·2DMAP$ (199.2–203.7 pm) [3] and also are in agreement with those reported for $Zn(OCOCH_3)_2·2NC_5H_5$ [10].

2.2.2. Bis(4-dimethylaminopyridine)cadmium bis(trifluoroacetate), $Cd(OCOCF_3)_2·2DMAP$

To our knowledge, two single crystal structures of cadmium trifluoroacetate complexes have been reported so far [12,13]. While the Cd atom in $[Cd(OCOCF_3)_2·PPh_3]_2$ is penta-coordinated by four bridging trifluoroacetate groups and one terminal PPh_3 ligand [12], the molecular structure of $Cd(OCOCF_3)_2·2(1,10\text{-phenanthroline})$ is suggested to show hepta-coordination around the cadmium atom [13].

$Cd(OCOCF_3)_2·2DMAP$ (Table 2, Figs. 2 and 3) has a crystallographically imposed inversion center of symmetry. The cadmium atom is distorted octahedrally surrounded by four equatorial oxygen atoms, two deriving from two bridging units and two from one chelating moiety, and two nitrogen atoms of the DMAP ligands occupying axial sites.

Cyclic dimeric units are built up forming eight-member rings of two cadmium atoms and two bridging trifluoroacetate groups. In the bridging CF_3COO unit, Cd–O distances are nearly equidistant (240.5 and 242.0 pm). The same is true for carbon–oxygen distances (123.1 and 124.8 pm; C 41–O 411(O 413)) emphasizing an ionic bridging character of this unit. Cd–O distances are significantly longer than those reported for $[Cd(OCOCF_3)_2·PPh_3]_2$ [12] (224.9–229.8 pm), again indicating the ionic character of the bridging $Cd–OCOCF_3$ units. Both Cd–O distances of the chelating CF_3COO group are of comparable size (244.7 and 247.5 pm), in this case indicating a bidentate unit.

The data presented in [13] might be interpreted as one “bidentate” (Cd–O distances 240.6 and 282.0 pm [13*]) and one monodentate trifluoroacetate group (234.3 pm (“second contact”, 328.0 pm [13*] (402.1 pm, [13])). All C–O bond lengths of 123.1–125.2 pm indicate ionic trifluoroacetate groups [13], in every case with the $[Cd(DMAP)_2]^{2+}$ group acting as the cation. Cd–N contacts (223.9 pm) are shorter than those reported for $[Cd(NCSe)_2·2DMAP]_n$ and $Cd(NCS)_2·2DMAP$ (232.4 and 282.5 pm) [3].

With respect to the quasi-linear N–Cd–N moiety (171.1°), N–Cd–O angles deviate from the right angle by less than 5°. Geometry in the plane around Cd, built up by four oxygen contacts, is determined from two angles closely related to the right angle, one acute angle (O 311–Cd–O 312, 53.9°) for the bidentate trifluoroacetate group and one obtuse angle between the bridging trifluoroacetate groups (O 411–Cd–O 412′, 138.9°).

With respect to studies on the coordination behaviour of $Hg(OCOCF_3)_2$ with pyridine derivatives [14–16], the results of the molecular structure of $Cd(OCOCF_3)_2·2DMAP$ can be summarized as follows. The cationic unit $[Cd(DMAP)_2]^{2+}$ is surrounded by two ionic bridging trifluoroacetate groups and one symmetrically chelating ionic trifluoroacetate ligand. Dimeric units of eight-member rings are built up from the bridging moieties.

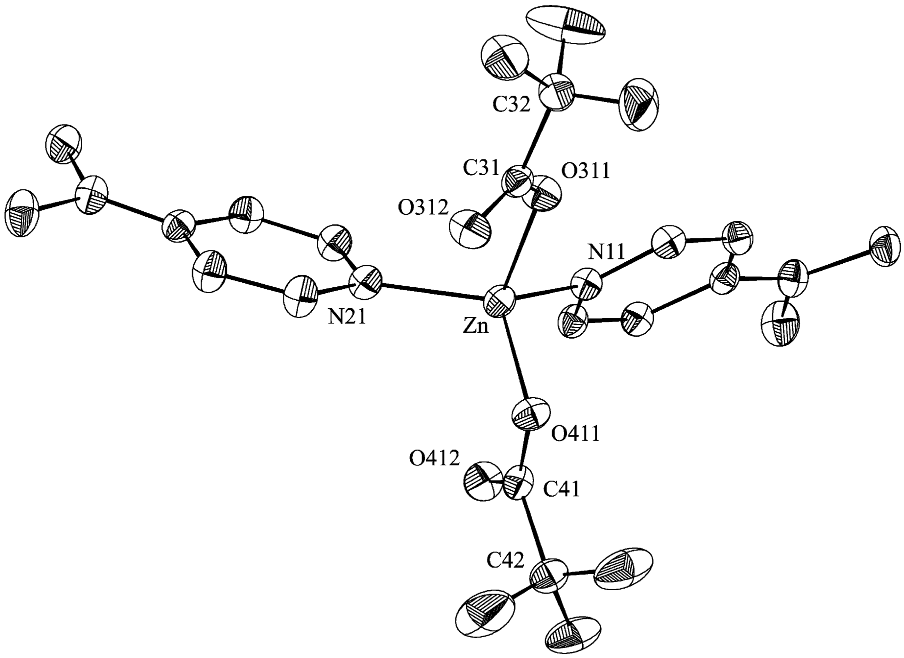

Fig. 1. Asymmetric unit of $Zn(OCOCF_3)_2 \cdot 2DMAP$ **I**. Coordination around Zn with the atomic labeling scheme. Thermal ellipsoids are shown at 50% probability.

2.2.3. *Bis(4-dimethylaminopyridine)mercury bis(trifluoroacetate), $[Hg(OCOCF_3)_2 \cdot 2DMAP] \cdot CH_3OH$*

$[Hg(OCOCF_3)_2 \cdot 2DMAP] \cdot CH_3OH$ (Table 2, Figs. 4 and 5) has a crystallographically imposed inversion center of symmetry similar to the cadmium derivative. The mercury atom is distorted octahedrally surrounded by four equatorial oxygen atoms—two deriving from two bridging units and two from one chelating moiety—and two nitrogen atoms of the DMAP ligands occupying axial sites. In comparison with data reported for $Hg(OCOCF_3)_2$ complexes ([14–16] and literature cited therein), exclusively ionic trifluoroacetate groups surround the mercury center. Different bonding modes as explained and described in [16] are not of significant interest in this case. All Hg–O bond lengths are significantly longer than 253 pm which is estimated as the ionic distance [16] between a Hg^{2+} ion [17] and the effective O radius in the trifluoroacetate group [18] indicating ionic trifluoroacetate groups [16]. In contrast with the structure of the cadmium derivative, the bidentate, chelating trifluoroacetate group is less symmetric. Distances are 262.7 and 280.0 pm, respectively.

With respect to the quasi-linear N–Hg–N moiety (172.9°), N–Hg–O angles deviate from the 90° angle by a maximum of 4.4°. Geometry in the plane around Hg, built up by four oxygen contacts, is determined from two angles related to the right angle (86.1 and 79.0°), one acute angle (O 311–Hg–O 312, 48.3°) for the bidentate trifluoroacetate group and one very obtuse angle between the bridging trifluoroacetate groups (O 412–Hg–O 411′, 146.6°).

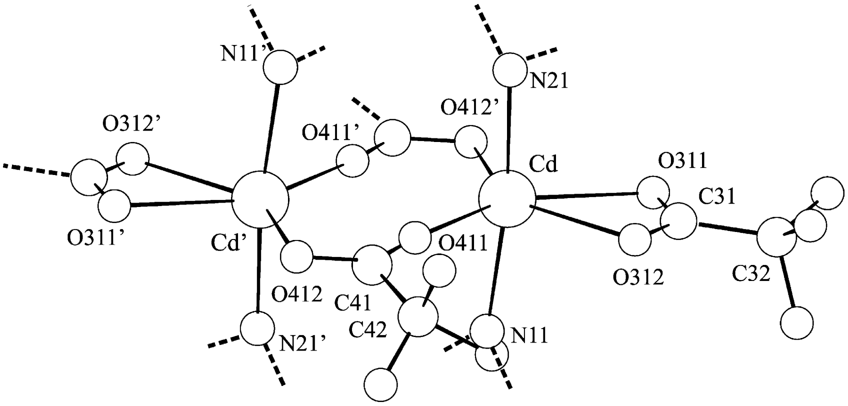

Fig. 2. $Cd(OCOCF_3)_2 \cdot 2DMAP$ **II**. Coordination around Cd with the atomic labeling scheme.

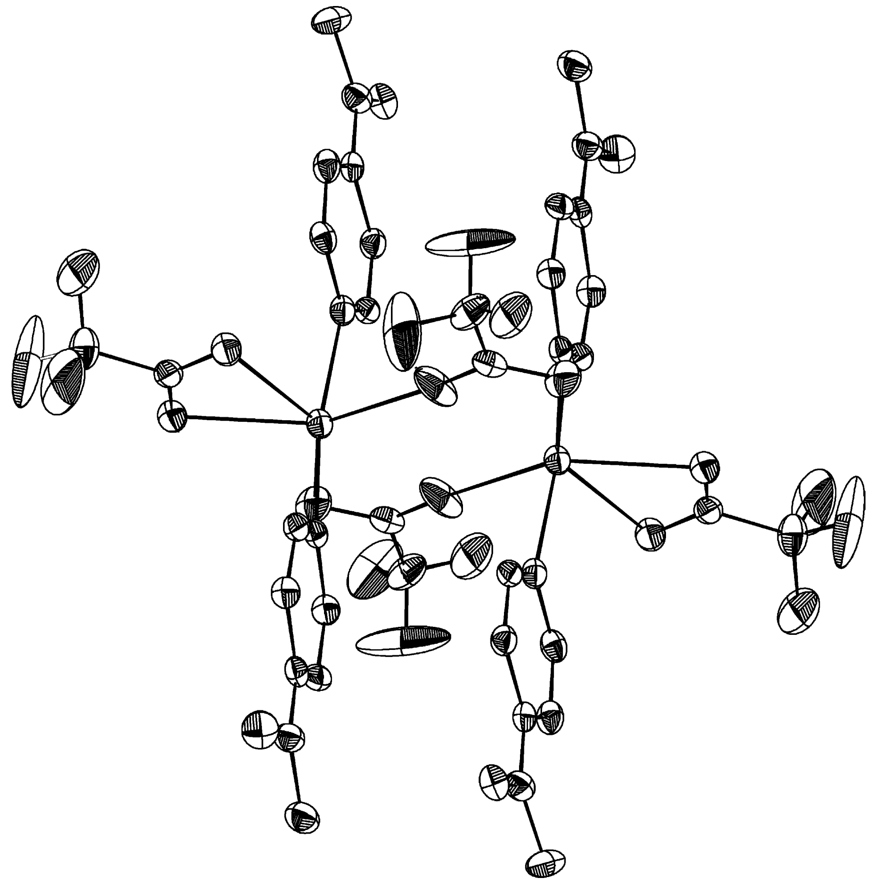

Fig. 3. Molecular structure of the $Cd(OCOCF_3)_2 \cdot 2DMAP$ dimer **II** with thermal ellipsoids at the 50% probability level.

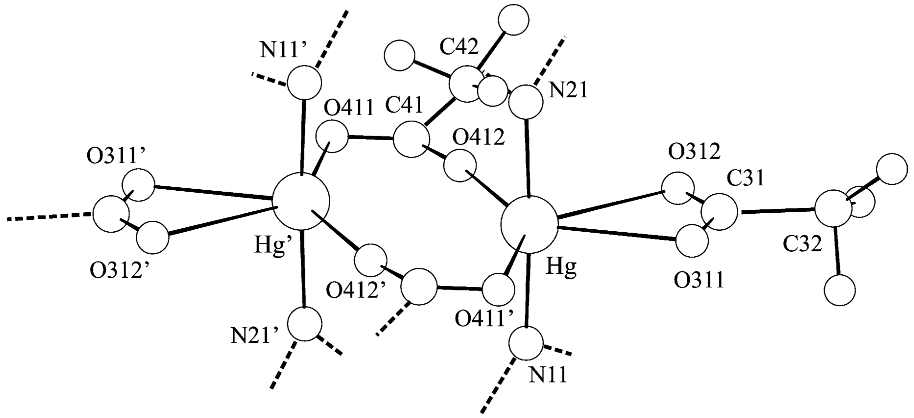

Fig. 4. $Hg(OCOCF_3)_2 \cdot 2$ DMAP **III**. Coordination around Hg with the atomic labeling scheme.

3. Experimental

All the reactions were carried out in ambient atmosphere in open glass beakers. NMR spectra were recorded on a Bruker AC 200 spectrometer operating at 200.1 MHz (^1H). External standards were used in all cases (^1H: Me_4Si; ^{19}F: CCl_3F). Mass spectra were run on a Finnigan MAT 95 spectrometer using the electron impact method (20 eV) in a temperature range of 25 and 300 °C. Intensities are referenced to the most intensive peak despite any isotope patterns. Visible decomposition points were determined in one-end open glass capillaries. CHN analyses were carried out with a Heraeus CHN Rapid apparatus. Elemental analyses were performed by literature procedures: Zn, Cd, Hg [19], F [20].

Trifluoroacetates were prepared according to the literature procedure for $Hg(OCOCF_3)_2$ [1]. 4-Dimethylaminopyridine was purchased from Merck-Schuchardt and used as received.

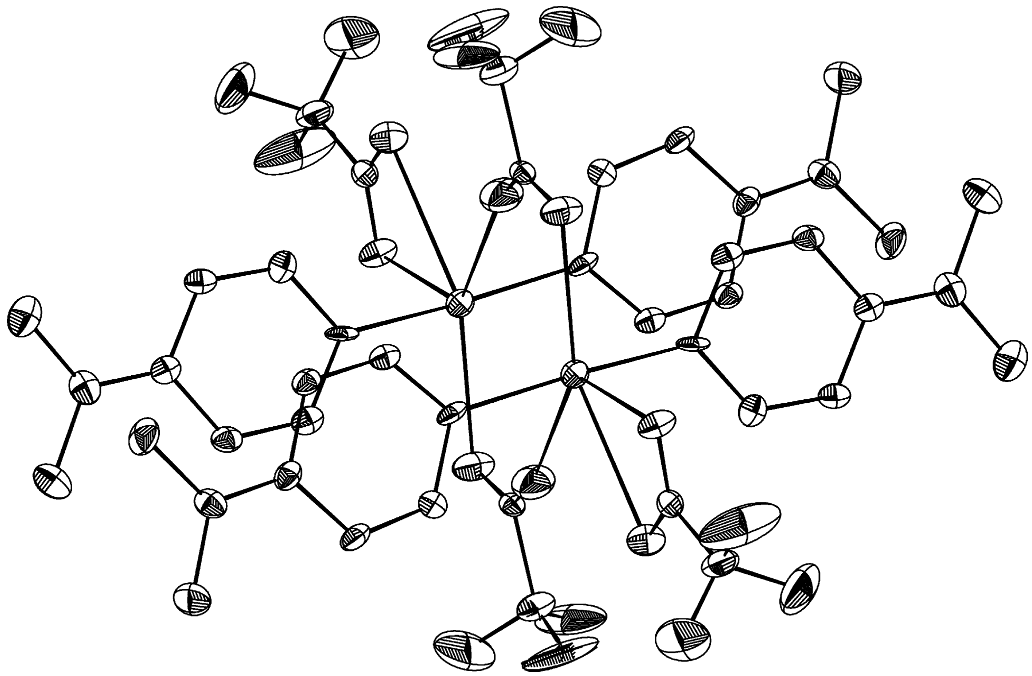

Fig. 5. Molecular structure of the $Hg(OCOCF_3)_2{\cdot}2DMAP$ dimer **III** with thermal ellipsoids at the 50% probability level.

3.1. Syntheses of $M(OCOCF_3)_2{\cdot}2DMAP$ (M = Zn, Cd, Hg)

$M(OCOCF_3)_2$ (5 mmol) were suspended in 10 ml methanol. DMAP (10 mmol) was added in one portion as a solid. Mixtures were heated until clear, colorless solutions were obtained and then cooled to ambient temperature. Colorless crystals of the title compounds precipitated in quantitative yields after evaporating methanol overnight under a ventilated hood.

Single crystals were grown on slowly cooling saturated hot solutions of the appropriate compounds to room temperature; $Zn(OCOCF_3)_2{\cdot}2DMAP$ and $Hg(OCOCF_3)_2{\cdot}2DMAP$ from methanol, $Cd(OCOCF_3)_2{\cdot}2DMAP$ from dichloromethane.

^{19}F NMR spectra of all compounds (CD_3OD) displayed exclusively one signal for the trifluoroacetate group at approximately −75 ppm. ^1H NMR chemical shifts deviated only slightly from those of neat DMAP. Results of NMR spectra were unsatisfactory with respect to structural information.

EI mass spectra (ca. 120 °C) of $Zn(OCOCF_3)_2{\cdot}2DMAP$ and $Cd(OCOCF_3)_2{\cdot}2DMAP$ exclusively showed the peak of $[C_7H_{10}N_2]^+$ under comparable conditions. At elevated temperature in the case of $Cd(OCOCF_3)_2{\cdot}2DMAP$ also peaks for $[CdOCOCF_3]^+$ and $[Cd]^+$ were detected. Mass spectra of the mercury derivative exhibited the ions $[CF_3Hg]^+$, $[Hg]^+$, $[CF_3]^+$ and $[CO_2]^+$ besides the DMAP peak.

Neither NMR and mass spectra nor IR analyses gave any further insight into the molecular structure of these derivatives. Relevant stretching modes of the trifluoroacetate group [2] and stretching frequencies of the DMAP unit [3] superpose, not giving any kind of information about the bonding mode of the trifluoroacetate group.

3.1.1. Bis(4-dimethylaminopyridine)zinc bis(trifluoroacetate), $Zn(OCOCF_3)_2{\cdot}2DMAP$

Colorless needles: mp 130 °C (beginning decomposition). EIMS 20 eV, *m/z* (relative intensity): 122 $[C_7H_{10}N_2]^+$ (100).

IR (KBr) ν: 3443 (s, br), 2924 (m), 1682 (vs), 1620 (vs), 1547 (s), 1447 (s), 1397 (s), 1296 (m), 1227 (vs), 1134 (s), 1069 (s), 1017 (vs), 947 (m), 839 (s), 818 (s), 760 (m), 723 (s), 530 (m).

Anal. Calcd. for $C_{18}H_{20}N_4O_4F_6Zn$: C, 40.4; H, 3.8; N, 10.5; F, 21.3; Zn, 12.2. Found: C, 40.2; H, 3.9; N, 10.2; F, 22.6; Zn, 11.7.

3.1.2. Bis(4-dimethylaminopyridine)cadmium bis(trifluoroacetate), $Cd(OCOCF_3)_2{\cdot}2DMAP$

Colorless needles: mp 180 °C (beginning decomposition). EIMS 20 eV, *m/z* (relative intensity): 122 $[C_7H_{10}N_2]^+$ (100).

IR (KBr) ν: 3436 (s, br), 2920 (m), 1682 (vs), 1618 (vs), 1545 (s), 1447 (s), 1397 (s), 1294 (m), 1225 (vs), 1130 (s), 1065 (s), 1011 (vs), 947 (m), 837 (s), 816 (s), 760 (m), 723 (s), 532 (m).

Anal. Calcd. for $C_{18}H_{20}N_4O_4F_6Cd$: C, 37.1; H, 3.5; N, 9.6; F, 19.6; Cd, 19.3. Found: C, 35.3; H, 4.0; N, 8.9; F, 20.8; Cd, 19,0.

3.1.3. Bis(4-dimethylaminopyridine)mercury bis(trifluoroacetate), $Hg(OCOCF_3)_2{\cdot}2DMAP$ (crystal with 1 eq. CH_3OH)

Colorless needles: mp 216–220 °C (decomposition). EIMS 20 eV, *m/z* (relative intensity): 271 $[CF_3Hg]^+$ (18); 202 $[Hg]^+$ (29); 122 $[C_7H_{10}N_2]^+$ (36); 69 $[CF_3]^+$ (44); 44 $[CO_2]^+$ (100).

IR (KBr) ν: 3451 (s, br), 2926 (m), 1682 (vs), 1615 (vs), 1537 (s), 1447 (s), 1393 (s), 1343 (m), 1294 (m), 1223 (vs), 1137 (s), 1065 (s), 1007 (vs), 947 (m), 837 (s), 812 (s), 756 (m), 723 (s), 529 (m).

Anal. Calcd. for $C_{19}H_{24}N_4O_5F_6Hg$: F, 16.2; Hg, 28.5. Found: F, 17.1; Hg, 27.8.

3.2. Single crystal structure determinations

A suitable single crystal of each compound was carefully selected under a polarizing microscope and mounted in glass capillaries. The scattering intensities were collected by an imaging plate diffractometer (IPDS II; STOE and CIE) equipped with a normal focus, 1.75 kW, sealed tube X-ray source (Mo Kα, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. Intensity data for $Zn(OCOCF_3)_2{\cdot}2DMAP$ (**I**) were collected at 170 K in 165 frames with ω scans ($0 \leq \omega \leq 180°$; $\psi = 0°$, $0 \leq \omega \leq 150°$; $\psi = 90°$, $\Delta\omega = 2°$, exposure time of 5 min) in the 2θ range of 2.3–59.5°. The intensity data for $Cd(OCOCF_3)_2{\cdot}2$ DMAP (**II**) and $[Hg(OCOCF_3)_2{\cdot}2DMAP]{\cdot}CH_3OH$ (**III**) were collected at 170 K in 135 frames with ω scans ($0 \leq \omega \leq 180°$; $\psi = 0°$, $0 \leq \omega \leq 90°$; $\psi = 90°$, $\Delta\omega = 2°$, exposure time of 8 min for **II** and 5 min for **III**) in the 2θ range of 1.9–54.8°. The structures were solved by direct methods (program SHELXS-97 [21]) and refined by the full-matrix least-squares method on all $|F^2|$ data using the SHELXL-93 [22] program. For $[Hg(OCOCF_3)_2{\cdot}2DMAP]{\cdot}CH_3OH$ (**III**) the C and O atom in the solvate molecule is disordered; the occupancy factor for each was refined, resulting in value of 0.50(4) for C 1 and 0.42(3) for O 1. H atom positions for **I** and **II** were taken from the difference Fourier card at the end of the refinement. For compound **III** H atoms were not included in the refinements. A numerical absorption correction was applied after optimization of the crystal shape (X-RED [23] and X-SHAPE [24]). The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all of the hydrogen atoms (except compound **III**). Details of the refinements are given in Table 1.[1] Selected internuclear distances and angles are presented in Table 2.

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References

[1] W.A. Herrmann, G. Brauer (Eds.), Synthetic methods of organometallic and inorganic chemistry, in: D.K. Breitinger, W.A. Herrmann (Eds.), Copper, Silver, Gold, Zinc, Cadmium, Mercury, vol. 5, Georg Thieme, Stuttgart, New York, 1999, pp. 221–223.
[2] G.B. Deacon, R.J. Phillips, Coord. Chem. Rev. 33 (1980) 227–250.
[3] P.M. Secondo, J.M. Land, R.G. Baughman, H.L. Collier, Inorg. Chim. Acta 309 (2000) 13–22.
[4] B. Bovio, A. Cingolani, C. Pettnari, G.G. Lobbia, F. Bonati, Z. Anorg. Allg. Chem. 602 (1991) 169–177.
[5] D.B. Dell'Amico, D. Boschi, F. Calderazzo, L. Labella, F. Marchetti, Inorg. Chim. Acta 330 (2002) 149–154.
[6] B.-H. Ye, F. Xue, G.-Q. Xue, L.-N. Ni, T.C.W. Mak, Polyhedron 18 (1999) 1785–1790.
[7] W. Yang, H. Schmider, Q. Wu, Y.-S. Zhang, S. Wang, Inorg. Chem. 39 (2000) 2397–2404.
[8] E.J. Corey, K. Shimoji, Tetrahedron Lett. 24 (1983) 169–172.
[9] R. Battistuzzi, G. Peyronel, Polyhedron 2 (1983) 471–474.
[10] B. Singh, J.R. Long, F. Fabrizi di Biani, D. Gatteschi, P. Stavropoulos, J. Am. Chem. Soc. 119 (1997) 7030–7047.
[11] A. Bondi, J. Phys. Chem. 68 (1964) 441–451.
[12] T. Allman, R.C. Goel, N.K. Jha, A.L. Beauchamp, Inorg. Chem. 23 (1984) 914–918.
[13] S. Sen, M.K. Sumar, P. Kundu, S. Mitra, C. Kruger, J. Bruckmann, Inorg. Chim. Acta 288 (1999) 118–131 (13*: CCDC 116770).
[14] J. Halfpenny, R.W.H. Small, F.G. Thorpe, Acta Cryst. B 34 (1978) 3075–3077.
[15] J. Halfpenny, R.W.H. Small, Acta Cryst. B 34 (1978) 3758–3760.
[16] J. Halfpenny, R.W.H. Small, Acta Cryst. C 53 (1997) 438–443.
[17] D. Grdenic, Q. Rev. Chem. Soc. 19 (1965) 303–328.
[18] L. Golic, J.C. Speakman, J. Chem. Soc. (1965) 2530–2542.
[19] Komplexometrische Methoden mit Titriplex, Merck, Darmstadt.
[20] A.D. Campbell, P.A. Dawson, Mikrochim. Acta (Wien) I (1983) 489–494.
[21] G.M. Sheldrick, SHELXS-97-Program for Structure Analysis, Göttingen, (1998).
[22] G.M. Sheldrick, SHELXL-93-Program for Crystal Structure Refinement, Göttingen (1993).
[23] X-RED 1.22, Stoe Data Reduction Program (C) 2001 Stoe & Cie GmbH Darmstadt.
[24] X-SHAPE 1.06, Crystal Optimization for Numerical Absorption Correction (C) 1999 STOE & Cie GmbH, Darmstadt.

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[1] Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 186637 for $Zn(OCOCF_3)_2{\cdot}2DMAP$, CCDC 186638 for $Cd(OCOCF_3)_2{\cdot}2DMAP$ and CCDC 186639 for $[Hg(OCOCF_3)_2{\cdot}2DMAP]{\cdot}CH_3OH$. Copies of the data can be obtained, free of charge, on application to CHCO, 13 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1323-336033 or e-mail: deposit@ccdc.cam.ac.uk).