# Reversible Gas−Solid Reactions between the Organometallic Zwitterion [($\eta^5$-C$_5$H$_4$COOH)($\eta^5$-C$_5$H$_4$COO)Co$^{III}$] and Vapors of Trifluoroacetic and Tetrafluoroboric Acids

Dario Braga,*,† Gianna Cojazzi,‡ Dario Emiliani,† Lucia Maini,† and Fabrizia Grepioni*,§

*Dipartimento di Chimica G. Ciamician, Università di Bologna, Via Selmi 2, 40126 Bologna, Italy, Centro CNR per la Fisica delle Macromolecole, c/o Dipartimento di Chimica G. Ciamician, Via Selmi 2, 40126 Bologna, Italy, and Dipartimento di Chimica, Università di Sassari, Via Vienna 2, 07100 Sassari, Italy*

*Summary: Exposure of the solid zwitterion [($\eta^5$-C$_5$H$_4$-COOH)($\eta^5$-C$_5$H$_4$COO)Co$^{III}$] (**1**) to vapors of CF$_3$COOH and HBF$_4$ quantitatively produces the corresponding salts of the cation [($\eta^5$-C$_5$H$_4$COOH)$_2$Co$^{III}$]$^+$ (**2**), namely **2**[CF$_3$COO] and **2**[BF$_4$]. Both heterogeneous reactions are fully reversible; the acids can be quantitatively removed by mild thermal treatment, which regenerates the starting material. Single crystals of **2**[CF$_3$COO] and **2**[BF$_4$] for X-ray diffraction can be obtained if the same reaction is carried out in solution. They possess the same structures as those produced in the gas−solid reactions.*

## Introduction

Solid−gas reactions between acids and bases are well-known, though they have been extensively studied mainly in the field of organic solid-state chemistry.[1] Phase reconstructions upon transformations of solid reagents into the product crystals have been investigated in the case of many reactions between organic solids and small molecules,[2a] such as ClCN and BrCN,[2b] and amines.[2c] Other reactions with gases are also known.[3]

Heterogeneous reactions involving organometallic species are much less common. In a seminal study, van Koten has recently shown that organoplatinum(II) complexes containing N,C,N tridentate coordinating anion "pincers" reversibly bind gaseous SO$_2$ in the solid state, leading to quantitative adduct formation.[4]

To the best of our knowledge, however, the possibility of exploiting the amphoteric behavior of an organometallic molecule to react, reversibly, with vapors of either acids or bases has never been explored before.

Recently, we have discovered that crystals of the organometallic zwitterion [($\eta^5$-C$_5$H$_4$COOH)($\eta^5$-C$_5$H$_4$-COO)Co$^{III}$] (**1**) reversibly react with hydrated vapors of HCl and ammonia, to yield the corresponding hydrated chloride [($\eta^5$-C$_5$H$_4$COOH)$_2$Co$^{III}$]Cl·H$_2$O and ammonium [($\eta^5$-C$_5$H$_4$COO)$_2$Co$^{III}$][NH$_4$]·3H$_2$O salts, which have been fully characterized in the solid state by single-crystal and powder X-ray diffraction, IR spectroscopy, and thermogravimetry.[5]

The zwitterion [($\eta^5$-C$_5$H$_4$COOH)($\eta^5$-C$_5$H$_4$COO)Co$^{III}$] can be quantitatively prepared[5,6a] from the corresponding dicarboxylic cationic acid [($\eta^5$-C$_5$H$_4$COOH)$_2$Co$^{III}$]$^+$, which we are extensively investigating because of the peculiar combination of ionic charge and removable protons that makes it particularly interesting in crystal engineering studies.[6] Indeed, the amphoteric behavior of **1** is due to its zwitterionic nature, which, in turn, depends on the presence of one "proton loaded" −COOH group (able to react with bases) and one "unloaded" −COO$^-$ group (able to react with acids).

In this paper we describe two novel heterogeneous gas−solid reactions between crystalline **1** and vapors of CF$_3$COOH and HBF$_4$. Acid vapors are taken up quantitatively, generating the corresponding salts of the protonated product of **1**, namely the cation [($\eta^5$-C$_5$H$_4$-COOH)$_2$Co$^{III}$]$^+$ (**2**), yielding **2**[CF$_3$COO] and **2**[BF$_4$]. Importantly, both heterogeneous reactions are fully reversible and the acids can be quantitatively removed by mild thermal treatment, which regenerates the starting material. Besides investigating the heterogeneous reactions, we report the full structural characterization of the products both as single crystals and as polycrystalline powders. Single crystals of **2**[CF$_3$COO]

* To whom correspondence should be addressed. E-mail: D.B., dbraga@ciam.unibo.it; F.G., grepioni@ssmain.uniss.it. Fax: D.B., int +39-051-2099456; F.G., int +39-079-212069.
† Università di Bologna.
‡ Centro CNR per la Fisica delle Macromolecole.
§ Università di Sassari.

(1) (a) Miller, R. S.; Curtin, D. Y.; Paul, I. C. *J. Am. Chem. Soc.* **1974**, *96*, 6340. (b) Miller, R. S.; Paul, I. C.; Curtin, D. Y. *J. Am. Chem. Soc.* **1974**, *96*, 6334. (c) Chiang, C. C.; Lin, C.-T.; Wang, A. H.-J.; Curtin, D. Y.; Paul, I. C. *J. Am. Chem. Soc.* **1977**, *99*, 6303. (d) Paul, I. C.; Curtin, D. Y. *Science* **1975**, *187*, 19.

(2) (a) Kaupp, G.; Kuse, A. *Mol. Cryst. Liq. Cryst.* **1998**, *313*, 36. (b) Kaupp, G. *Mol. Cryst. Liq. Cryst.* **1994**, *242*, 153. (c) Kaupp, G. In *Comprehensive Supramolecular Chemistry;* Davies, J. E. D., Ed.; Elsevier: Oxford, U.K., 1996; Vol. 8, p 381. (d) Kaupp, G.; Schmeyers, J.; Boy, J. *Chem. Eur. J.* **1998**, *4*, 2467. (e) Kaupp, G.; Schmeyers, J.; Boy, J. *Tetrahedron* **2000**, *56*, 6899. (f) Kaupp, G.; Schmeyers, J.; Haak, M.; Marquardt, T.; Herrmann, A. *Mol. Cryst. Liq. Cryst.* **1996**, *276*, 315.

(3) (a) Tanaka, K.; Toda, F. *Chem. Rev.* **2000**, *100*, 1025 and references therein. (b) Tanaka, K.; Fujimoto, D.; Oeser, T.; Irngartinger, H.; Toda, F. *Chem. Commun.* **2000**, 413.

(4) (a) Albrecht, M.; Gossage, R. A.; Lutz, M.; Speck, A. L.; van Koten, G. *Chem. Eur. J.* **2000**, *6*, 1431. (b) Albrecht, M.; Lutz, Schreurs, A. M. M.; Lutz, E. T. H.; M.; Speck, A. L.; van Koten, G. *J. Chem. Soc., Dalton Trans.* **2000**, 3797.

(5) Braga, D.; Cojazzi, G.; Emiliani, D.; Maini, L.; Grepioni, F. *Chem. Commun.* **2001**, 2272.

(6) (a) Braga, D.; Maini, L.; Polito, M.; Grepioni, F. *Organometallics* **1999**, *18*, 2577. (b) Braga, D.; Maini, L.; Polito, M.; Rossini, M.; Grepioni, F. *Chem. Eur. J.* **2000**, *6*, 4227.

and **2**[BF$_4$] have been obtained by carrying out the same reactions in solution. By comparison of calculated and measured powder diffractograms it has been shown that they possess the same structures as the salts produced in the gas−solid reactions.

## Results and Discussion

The organometallic zwitterion **1** is easy to handle, and it is thermally stable up to a temperature of 506 K. Complete conversion of neutral crystalline **1** (1−10 mg) into the crystalline salts **2**[CF$_3$COO] and **2**[BF$_4$] is attained in 1 and 16 h, respectively, on exposure to vapors of CF$_3$COOH (99%) and of a diethyl ether solution of HBF$_4$ (54%) (see the Experimental Section).

Quantitative formation of **2**[CF$_3$COO] and **2**[BF$_4$] upon vapor uptake is easily assessed by comparing the X-ray powder diffraction patterns measured on the polycrystalline products after reaction with those calculated on the basis of the single-crystal structures (see below). Crystalline **2**[CF$_3$COO] and **2**[BF$_4$] can be converted back to **1** by heating the samples for 30 min at 170 °C in an oil bath under low pressure (10$^{-5}$ atm); the powder diffractogram of the final product corresponds precisely to that of form **1**. Crystalline **1** can be cycled through several absorption and release processes without decomposition or detectable formation of amorphous material. Conversion of the zwitterionic form **1** into the dicarboxyl form **2** in the heterogeneous reactions can also be easily monitored by IR spectroscopy (see the Experimental Section).

To unambiguously identify the polycrystalline materials **2**[CF$_3$COO] and **2**[BF$_4$] after reaction, we sought a way to obtain single crystals of the two products. To this end, we carried out the same reactions *in solution* and obtained single crystals of **2**[CF$_3$COO] and of **2**[BF$_4$] suitable for X-ray diffraction (see the Experimental Section).

Figure 1 collects in a visual form all information on reactivity and structures. One can easily appreciate that the two reactions imply dramatic structural changes, which, also in view of their reversibility, constitute an intriguing aspect of these processes.

The formation of **2**[CF$_3$COO] from **1** requires that the intermolecular O−H- - -O bonds between protonated −COOH and deprotonated −COO$^-$ groups belonging to zwitterion molecules be replaced, upon reaction with [CF$_3$COOH], by $^+$O−H- - -O$^-$ interactions between the −COOH groups on the fully protonated organometallic cation [($\eta^5$-C$_5$H$_4$COOH)$_2$Co$^{III}$]$^+$ (**2**) and the [CF$_3$COO]$^-$ anion (see Figure 1). The crystal is thus composed of ion pairs in which the [CF$_3$COO]$^-$ anion "pinches" the two protonated −COOH groups on the organometallic moiety (O- - -O distances 2.583(10) and 2.568(10) Å). In terms of packing arrangement, the conversion of **1** into **2** requires substantial molecular rearrangements; note inter alia that the C$_5$H$_4$COO(H) ligand conformation passes from transoid in **1** to cisoid in **2** upon formation of the ion pair. The formation of **2**[BF$_4$], on the other hand, appears to imply more limited molecular motions. The chain present in **1**, with zwitterion molecules held together by COOH- - -OOC interactions, are maintained in **2** with formation of classical carboxylic rings (O- - -O = 2.623(3) Å). The transoid conformation of the −COO(H) groups is also retained.
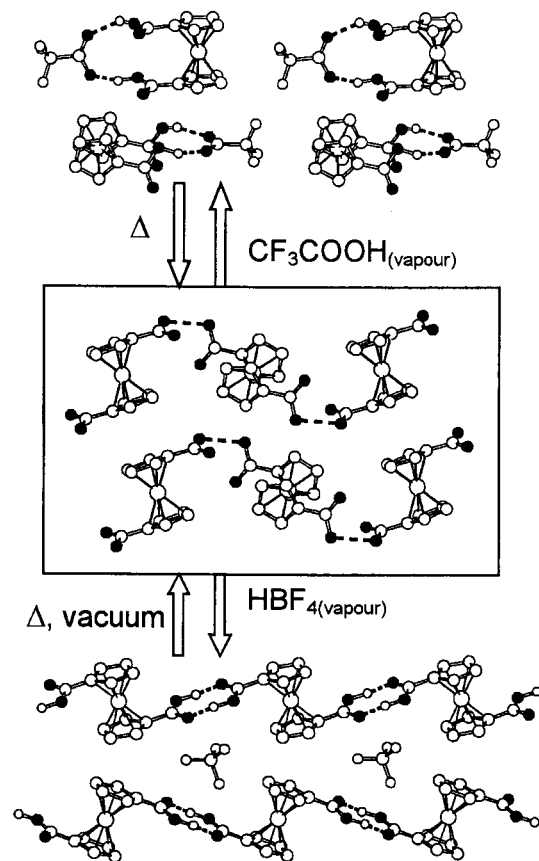


**Figure 1.** Structural relationship between the zwitterionic form **1** (middle), the ion pairs present in **2**[CF$_3$COO] (top), and the chains present in **2**[BF$_4$] (bottom). Note that the hydrogen-bonding interactions in this last compound imply two-proton carboxylic rings, while in **1** only one proton is involved. Note also how the transformation **1** ↔ **2**[CF$_3$COO]- requires complete reorientation of the Cp−COOH groups. The hydrogen atoms for **1**[6a] are not observed.

The same chain motif is present in the salt [($\eta^5$-C$_5$H$_4$-COOH)$_2$Co$^{III}$][PF$_6$][6b] and in the related bis(benzene)-chromium derivative [($\eta^6$-C$_6$H$_5$COOH)$_2$Cr$^I$][PF$_6$].[7] However, while in these latter crystals the parallel chains are related by translation, the chains in **2**[BF$_4$] are mirror images (see Figure 1), forming niches in which the small [BF$_4$]$^-$ anions are encapsulated. In both **2**[CF$_3$-COO] and **2**[BF$_4$] there is a large number of "charge assisted" C−H$^{\delta+}$- - -O$^{\delta-}$ and C−H$^{\delta+}$- - -F$^{\delta-}$ interactions between anions and cations.[8]

As mentioned above, powder diffraction was instrumental in unambiguously identifying the products of the heterogeneous reactions. The comparison between the powder patterns calculated on the basis of the single-crystal structures of **2**[CF$_3$COO] and **2**[BF$_4$] and those measured on the polycrystalline materials is shown in Figure 2, together with the experimental and calculated powder patterns of crystalline **1**. It is evident that the compounds obtained from the heterophase reactions possess the same solid-state structures as those obtained from solution. It should be stressed that this result could not be predicted a priori, since the crystal-

(7) Braga, D.; Maini, L.; Grepioni, F.; Elschenbroich, C.; Paganelli, F.; Schiemann, O. *Organometallics* **2001**, *20*, 1875.
(8) Grepioni, F.; Cojazzi, G.; Draper, S. M.; Scully, N.; Braga, D. *Organometallics* **1998**, *17*, 296.
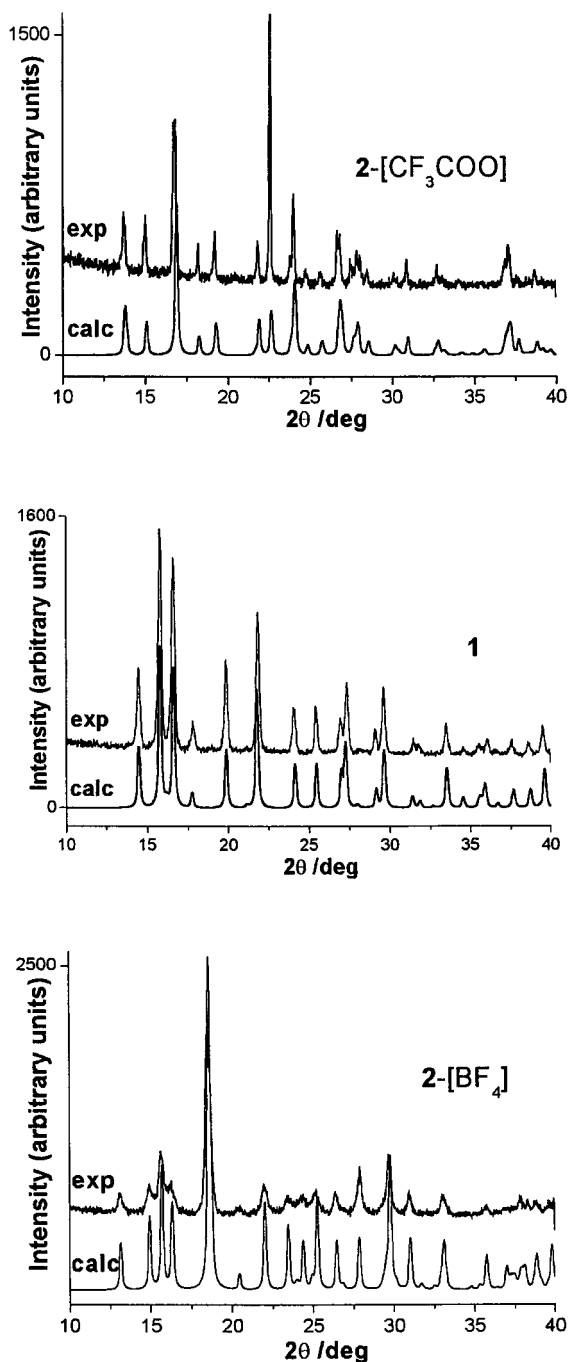
**Figure 2.** Comparison between the powder diffraction patterns measured on samples of **1** (center), **2**[CF$_3$COO] (top), and **2**[BF$_4$] (bottom) obtained in the heterogeneous reactions and those calculated on the basis of the single-crystal structures (see text).

lization from solution might lead to solvated species, as we have observed in many other cases.

## Conclusions

The deliberate engineering of a molecular solid that can perform a desired function is conceptually related to the construction of a supermolecule, whose collective functions and properties depend on the aggregation via *intermolecular* bonds of two or more component units.[9]

It is generally believed that molecular crystals held together only (or mainly) by hydrogen-bonding interactions cannot compete with covalent or ionic inorganic solids in terms of cohesion and stability. We have shown that exposure of the solid zwitterion [($\eta^5$-C$_5$H$_4$COOH)-($\eta^5$-C$_5$H$_4$COO)Co$^{III}$] (**1**) to vapors of CF$_3$COOH and HBF$_4$ quantitatively produces the corresponding salts of the cation [($\eta^5$-C$_5$H$_4$COOH)$_2$Co$^{III}$]$^+$ (**2**), namely **2**[CF$_3$COO] and **2**[BF$_4$]. The heterogeneous reactions are fully reversible, and the acids can be removed by thermal treatment, which quantitatively regenerates the starting material. The behavior of **1** toward vapors of CF$_3$-COOH and HBF$_4$ thus parallels that observed when **1** is exposed to hydrated HCl vapors.[5] Also in this latter case, when the acid−base reaction is carried out in solution, exactly the same products are obtained. The amphoteric behavior is, on the other hand, confirmed by the observation of similar reactions of **1** with vapors of bases, such as NH$_3$, NH$_2$Me, and NMe$_3$.[5]

In terms of crystal structure organization, formation of **2**[CF$_3$COO] and **2**[BF$_4$], besides leading from a formally neutral system to molecular salts, implies profound molecular rearrangements and breaking and forming of noncovalent interactions. From the analogy between gas−solid and solution reactions, one may be brought to suppose that the gas−solid reactions occur via a process of dissolution and recrystallization as the vapors are adsorbed by the crystalline powder. The reverse process, i.e. reconstruction of the zwitterion crystals, is more difficult to explain, as it implies proton removal from the cationic acid.

In summary, we have provided further evidence that heterogeneous gas−solid reactions can be a valid alternative to nanoporosity[10] for controlled uptake and release of small molecules, even though the processes involved are very different. While many nanoporous materials irreversibly decompose upon removal of guest molecules, our gas−solid reaction *exploits* the profound transformations associated with the reversible interconversion between a molecular crystal and a crystalline salt.

There are several open issues, which we plan to address soon. For instance, we need to explore the effect of particle size and surface on the *kinetics* of the reactions as well as the relationship between composition of the vapor phase and exposure time. The possibility of *anchoring* the zwitterionic unit to some *signaling* unit that, without altering the capacity of **1** to react with acids and bases, would allow us to exploit the amphoterism of **1** is also a fascinating prospect for the construction of versatile sensors. The bottom-up construction of solid-state sensors, filters, and sieves for small molecules is an attractive prospect for crystal engineering.[11]

(9) (a) Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375. (b) Braga, D.; Grepioni, F. *Acc. Chem. Res.* **2000**, *33*, 601.

(10) (a) Russell, V. A.; Evans, C. C.; Li, W.; Ward, M. D. *Science* **1997**, *276*, 575. (b) Holman, K. T.; Pivovar, A. M.; Swift, J. A.; Ward, M. D. *Acc. Chem. Res.* **2001**, *34*, 107. (c) Yaghi, O. M.; Li, G.; Li, H. *Nature* **1995**, *378*, 703. (d) Noro, S.-I.; Kitagawa, S.; Kondo, M.; Seki, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 2082. (e) Abrahams, B. F.; Hoskins, B. F.; Michail, D. M.; Robson, R. *Nature* **1994**, *369*, 727.

(11) (a) Zimmermann, S. C. *Science* **1997**, *276*, 543. (b) Janiak, C. *Angew. Chem., Int. Ed.* **1997**, *36*, 1431. (c) Rao, C. N. R.; Srinivasan, N.; Amitava, C.; Neeraj, S.; Ayi, A. A. *Acc. Chem. Res.* **2001**, *34*, 80. (d) Albrecht, M.; Lutz, M.; Speck, A. L.; van Koten, G. *Nature* **2000**, *406*, 970.

## Experimental Section

**General Comments.** The zwitterion **1** has been prepared as previously reported.[6] $CF_3COOH$ and $HBF_4$ were purchased from Aldrich and used without any further purification. Exposure to the acid vapors was attained by allowing the vapors of the corresponding solutions (10 mL) contained in a round-bottom flask to pass into a filter funnel, in which a glass sample holder containing powder **1** was placed. In this way the powder and the solution were not in contact; the reaction took place in a closed system.

**Synthesis of 2[CF₃COO] and 2[BF₄].** Two separate samples (10 mg each) of polycrystalline powder **1** are exposed to vapors of $CF_3COOH$ (99%) or $HBF_4$ (54% in diethyl ether) with the apparatus described above. Full conversion to **2**[$CF_3$-COO] and **2**[$BF_4$] is achieved after 1 and 16 h, respectively. IR spectra in KBr show that, upon reaction, the CO stretching at 1714 (s) $cm^{-1}$, characteristic of the zwitterionic form **1**, is replaced in **2**[$BF_4$] by bands at ca. 1734 (s) and 1707 (s) $cm^{-1}$ (as observed in the case of **2**Cl·$H_2O^5$), while in **2**[$CF_3COO$] a band at 1724 (s) $cm^{-1}$ is observed for the organometallic acid **2** and a band at 1607 (s) $cm^{-1}$ [12] for the $COO^-$ group belonging to the $CF_3COO^-$ anion. Treatment of both **2**[$CF_3COO$] and **2**[$BF_4$] at 170 °C and under vacuum ($10^{-5}$ atm) for 30 min quantitatively converts them back to **1**. Anal. Calcd for **2**[$CF_3$-COO] ($C_{14}H_{10}CoF_3O_6$, 390.15): C, 43.10; H, 2.58. Found: C, 42.88; H, 2.61. Calcd for **2**[$BF_4$] ($C_{12}H_{10}BCoF_4O_4$, 363.94): C, 39.60; H, 2.77. Found: C, 39.18; H, 2.75.

**Crystal Structure Determination of Compounds 2[CF₃COO] and 2[BF₄].** Single crystals of **2**[$CF_3COO$] and **2**[$BF_4$] were obtained by slow evaporation in the air of a solution of **1** in $CF_3COOH$ (99%) and $HBF_4$ (54% in diethyl ether), respectively. Crystal data and details of measurements for **2**[$CF_3COO$] and **2**[$BF_4$] are summarized in Table 1. The following details of the structure determination are common to both compounds: Mo Kα radiation, $\lambda = 0.710\ 73$ Å, graphite monochromator, $\psi$-scan absorption correction. All non-H atoms were refined anisotropically. $H_{COOH}$ atoms were directly located from Fourier maps and not refined. The $CF_3$ group belonging to the anion in **2**[$CF_3COO$] and the [$BF_4$]$^-$ anion in **2**[$BF_4$] are both disordered over two positions; the different orientations were refined with 50:50 occupancy ratios for the F atoms. H atoms bound to C atoms were added in calculated positions. The computer program SHELX97[13a] was used for structure solution and refinement. The computer program SCHAKAL99[13b] was used for all graphical representations. Hydrogen-bonding interactions were evaluated by the program PLATON.[13c] Correspondence between the structures determined by single-crystal X-ray diffraction and those of the bulk materials precipitated from solution was confirmed by comparing the experimental powder diffractograms obtained from the bulk

---

(12) Erroneously reported as 1707 $cm^{-1}$ in ref 5.

**Table 1.  Crystal Data and Details of Measurements for 2[CF₃COO] and 2[BF₄]**

|  | **2**[CF₃COO] | **2**[BF₄] |
|---|---|---|
| formula | $C_{14}H_{10}CoF_3O_6$ | $C_{12}H_{10}BCoF_4O_4$ |
| $M_w$ | 390.15 | 363.94 |
| $T$ (K) | 293(2) | 293(2) |
| cryst syst | orthorhombic | monoclinic |
| space group | $Pna2_1$ | $C2/c$ |
| $a$ (Å) | 14.919(5) | 12.438(4) |
| $b$ (Å) | 12.783(2) | 9.484(3) |
| $c$ (Å) | 7.393(2) | 11.400(3) |
| $\alpha$ (deg) | 90 | 90 |
| $\beta$ (deg) | 90 | 107.42(2) |
| $\gamma$ (deg) | 90 | 90 |
| $V$ (Å³) | 1409.9(6) | 1283.1(7) |
| $Z$ | 4 | 4 |
| $F(000)$ | 784 | 728 |
| $\mu$(MoKα) (mm$^{-1}$) | 1.284 | 1.402 |
| no. of measd rflns | 1464 | 1345 |
| Flack param | 0.13(5) | |
| no. of unique rflns | 1341 | 1283 |
| no. of params | 210 | 107 |
| GOF on $F^2$ | 0.951 | 1.062 |
| R1 (on $F$, $I > 2\sigma(I)$) | 0.0395 | 0.0341 |
| wR2 (on $F^2$, all data) | 0.1252 | 0.1035 |

materials with those calculated on the basis of the single-crystal structures. Powder data were collected on a Philips PW-1710 automated diffractometer with Cu Kα radiation and a graphite monochromator. The program PowderCell 2.2[12d] was used for calculation of X-ray powder patterns.

**Supporting Information Available:** Figures giving ORTEP drawings and IR spectra and tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and H atom coordinates for **2**[$CF_3COO$] and **2**[$BF_4$]; crystallographic data are also available in CIF format for the two compounds. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for **2**[$CF_3COO$] and **2**[$BF_4$] have also been deposited with the Cambridge Crystallographic Data Centre.

OM010936W

---

(13) (a) Sheldrick, G. M. SHELX-97, Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany, 1997. (b) Keller, E. SCHAKAL99, Graphical Representation of Molecular Models; University of Freiburg, Freiburg, Germany, 1999. (c) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *A46*, C31. (d) PowderCell programmed by W. Kraus and G. Nolze (BAM Berlin), subgroups derived by Ulrich Müller (Gh Kassel).