

New Volatile Perfluorinated Amidine–Carboxylate Copper(II) Complexes as Promising Precursors in CVD and FEBID Methods

Methods

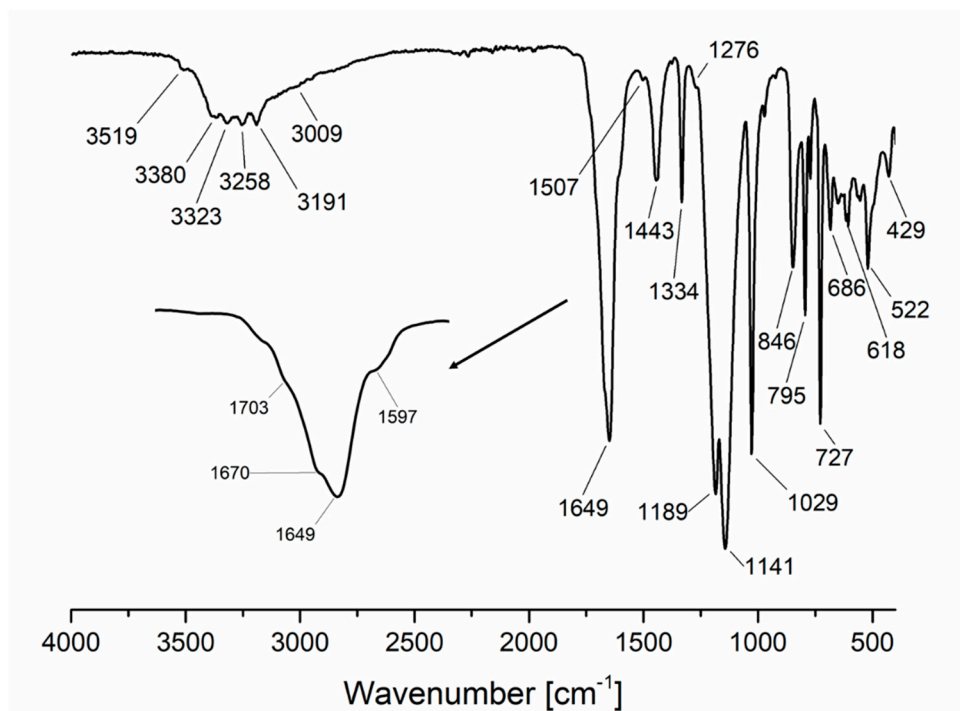


Figure S1. Infrared spectra for the complex $[\text{Cu}_2(\text{AMDH})_2(\mu\text{-O}_2\text{CF}_3)_4]$ (1).

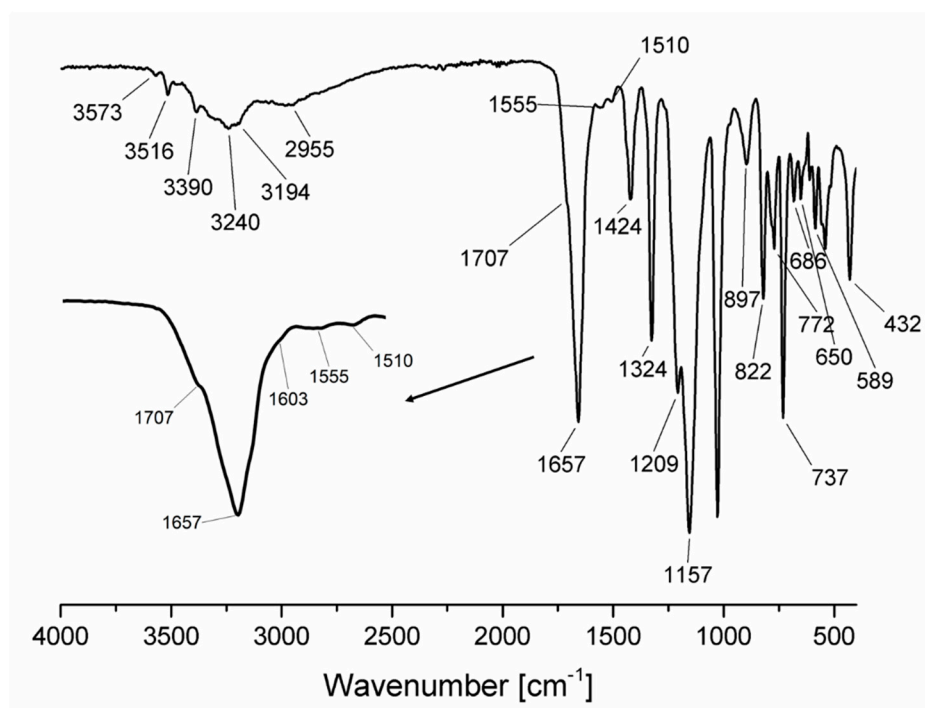


Figure S2. Infrared spectra for the complex $[\text{Cu}_2(\text{AMDH})_2(\mu\text{-O}_2\text{C}_2\text{F}_5)_4]$ (2).

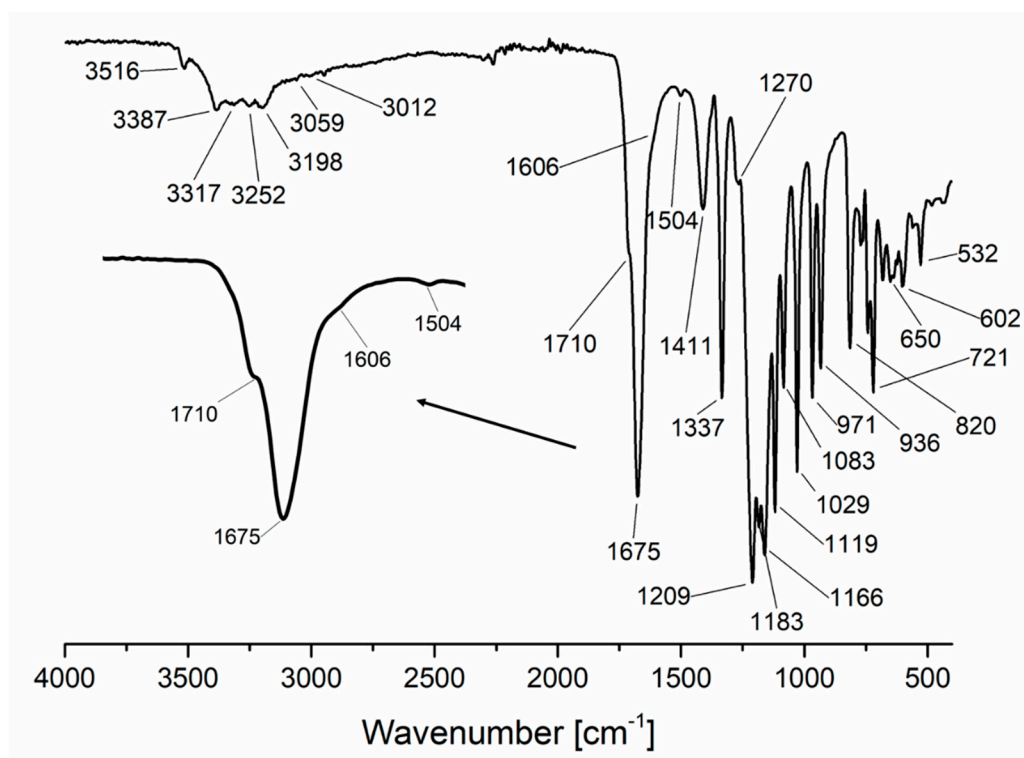


Figure S3. Infrared spectra for the complex $[\text{Cu}_2(\text{AMDH})_2(\mu\text{-O}_2\text{C}_3\text{F}_7)_4]$ (3).

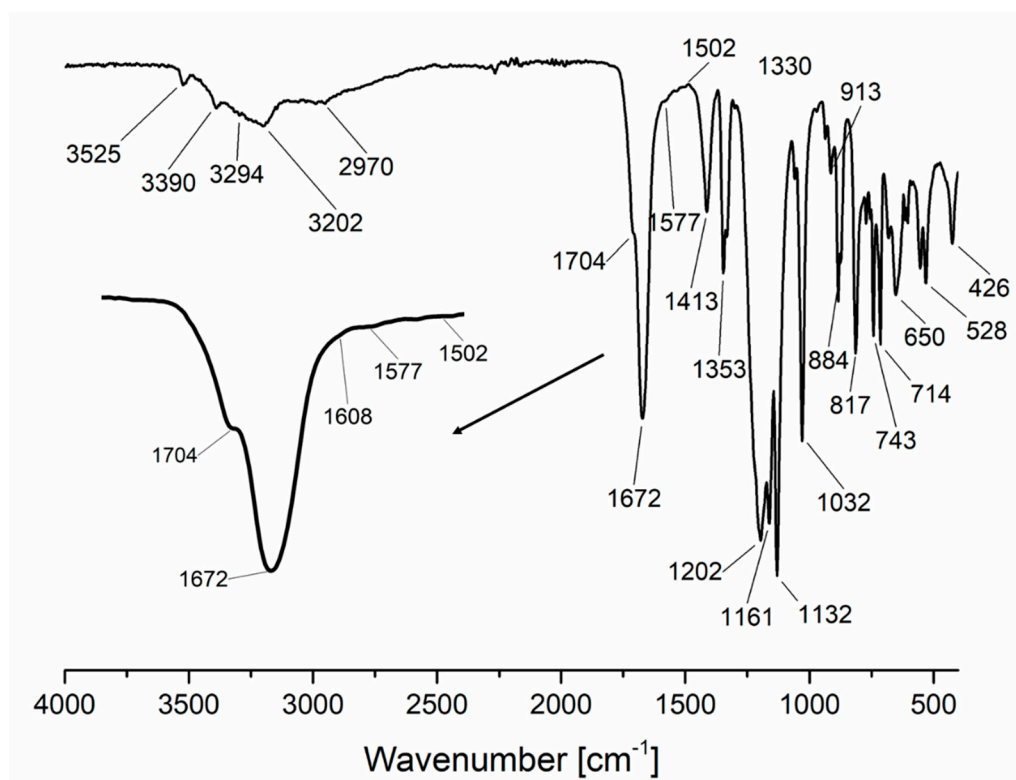


Figure S4. Infrared spectra for the complex $[\text{Cu}_2(\text{AMDH})_2(\mu\text{-O}_2\text{C}_4\text{F}_9)_4]$ (4).

Table S1. EI MS results for the complex [Cu₂(AMDH)₂(μ-O₂CF₃)₄] (1).

Fragments	m/z	Temperature [K]				
		313	357	396	426	538
[Cu ₂ (AMDH) ₂ (O ₂ CCF ₃) ₃] ⁺	789	4	13	67	2	-
[Cu ₂ (AMDH) ₂ (O ₂ CCF ₃) ₂] ⁺	676	<1	1	6	1	-
[Cu ₂ (AMD) ₂ (O ₂ CCF ₃) ₂] ⁺	674	<1	1	6	1	-
[Cu ₂ (NH ₂)(AMDH) ₂ (AMD)] ⁺	627	1	2	14	4	-
[Cu ₂ (NH ₂)(AMD) ₂ (O ₂ CCF ₃)] ⁺	577	-	<1	1	5	-
[Cu ₂ (AMD) ₂ (O ₂ CCF ₃)-H] ⁺	560	1	4	23	4	-
[Cu(AMDH) ₂ (O ₂ CCF ₃)] ⁺	500	6	16	82	3	-
[Cu ₂ (AMD) ₂] ⁺	448	1	3	29	12	-
[Cu ₂ (AMDH)(O ₂ CCF ₃)] ⁺	401	2	3	21	5	2
[Cu ₂ (AMD)(O ₂ CCF ₃)] ⁺	400	1	3	38	12	1
[Cu(AMDH) ₂] ⁺	387	3	6	30	2	<1
[Cu(AMDH)(AMD)] ⁺	386	6	14	71	5	<1
[Cu ₂ (O ₂ CCF ₃) ₂] ⁺	352	<1	1	6	2	38
[Cu(AMDH)(O ₂ CCF ₃)] ⁺	338	2	5	28	8	<1
[Cu ₂ (AMD)] ⁺	287	1	3	33	10	2
[Cu(AMDH)(HN=C=NH)] ⁺	267	6	10	39	7	<1
[Cu(AMD)(HN=C=NH)] ⁺	266	2	3	12	3	1
[Cu(AMD)(HCN)] ⁺	251	<1	1	3	22	<1
[Cu ₂ (O ₂ CCF ₃)] ⁺	239	1	4	27	11	74
[Cu(AMDH)] ⁺	225	11	24	100	46	<1
[AMDH] ⁺	162	55	41	1	84	<1
[C ₂ F ₅ CNH] ⁺	146	9	7	18	14	1
[Cu ₂ F] ⁺	145	1	1	7	4	23
[C ₂ F ₄ CNH] ⁺	127	12	8	18	19	4
[C ₂ F ₄ CN] ⁺	126	1	1	1	2	100
[C ₂ F ₅] ⁺	119	1	100	1	1	60
[C ₂ F ₄] ⁺	100	<1	52	95	100	36
[CO ₂] ⁺	44	7	2	1	1	6
[HN=C=NH] ⁺	42	48	23	60	42	12
[F ₂] ⁺	38	100	18	10	14	10

Table S2. EI MS results for the complex [Cu₂(AMDH)₂(μ-O₂C₃F₇)₄] (3).

Fragment	m/z	Temperature [K]				
		358	383	435	486	550
[Cu ₃ (O ₂ CC ₃ F ₇) ₅] ⁺	1256	-	-	1	5	1
[Cu ₃ (AMD)(O ₂ CC ₃ F ₇) ₄] ⁺	1204	-	-	1	4	-
[Cu ₂ (AMDH) ₂ (O ₂ CC ₃ F ₇) ₃] ⁺	1089	2	2	<1	<1	-
[Cu ₂ (AMDH)(O ₂ CC ₃ F ₇) ₃] ⁺	927	<1	2	2	3	-
[Cu ₂ (AMDH)(AMD)(O ₂ CC ₃ F ₇) ₂] ⁺	875	-	<1	-	-	-
[Cu ₂ (AMDH)(O ₂ CC ₃ F ₇) ₂] ⁺	714	-	<1	<1	1	-
[Cu ₂ (AMD)(O ₂ CC ₃ F ₇) ₃] ⁺	713	-	<1	<1	2	-
[Cu ₂ (AMD) ₂ (O ₂ CC ₃ F ₇) - H] ⁺	660	<1	<1	<1	1	-
[Cu(AMDH) ₂ (O ₂ CC ₃ F ₇) ₂] ⁺	600	2	3	1	<1	-
[Cu ₂ (O ₂ CC ₃ F ₇) ₂] ⁺	552	-	-	2	20	96
[Cu ₂ (AMDH)(O ₂ CC ₃ F ₇) ₂] ⁺	501	<1	1	3	6	<1
[Cu ₂ (AMD)(O ₂ CC ₃ F ₇) ₂] ⁺	500	<1	<1	5	34	<1
[Cu ₂ (AMDH) ₂] ⁺	450	<1	<1	2	7	<1
[Cu ₂ (AMD) ₂] ⁺	448	<1	<1	2	7	<1
[Cu(AMDH)(O ₂ CC ₃ F ₇) ₂] ⁺	438	<1	1	3	4	-
[Cu(AMDH)(AMD)] ⁺	386	1	2	<1	<1	<1
[Cu(AMD) ₂] ⁺	385	-	-	<1	2	5
[Cu ₃ (NH ₂) ₂ (AMD) - H] ⁺	383	-	<1	<1	3	4
[Cu ₂ (O ₂ CC ₃ F ₇) ₂] ⁺	339	-	<1	7	69	2
[Cu ₂ (AMD)] ⁺	287	<1	1	5	52	1
[Cu(HCN)(AMD)] ⁺	251	-	-	<1	20	<1
[Cu(AMDH)] ⁺	225	4	2	7	13	<1
[C ₃ F ₇] ⁺	169	18	26	37	1	1
[AMDH] ⁺	162	13	15	7	13	<1
[Cu ₂ F] ⁺	145	-	<1	13	18	97
[C ₂ F ₄ CN] ⁺	126	1	1	100	3	17
[C ₂ F ₅] ⁺	119	1	1	1	2	1
[C ₂ F ₄] ⁺	100	100	1	1	1	4
[CF ₂ CN] ⁺	76	1	1	1	1	50
[CO ₂ H] ⁺	45	30	42	34	100	47
[CO ₂] ⁺	44	3	3	2	2	4
[HN=C=NH] ⁺	42	14	11	7	8	2
[N≡C-NH] ⁺	41	1	100	55	19	1
[F ₂] ⁺	38	37	19	9	9	1

Table S3. EI MS results for the complex [Cu₂(AMDH)₂(μ-O₂C₄F₉)₄] (4).

Fragment	m/z	Temperature [K]				
		371	396	428	460	505
[Cu ₃ (AMDH)(O ₂ CC ₄ F ₉) ₅] ⁺	1668	-	<1	3	3	-
[Cu ₃ (O ₂ CC ₄ F ₉) ₅] ⁺	1506	-	-	2	14	16
[Cu ₃ (AMD)(O ₂ CC ₄ F ₉) ₄] ⁺	1404	-	-	2	17	4
[Cu ₄ (NH ₂) ₂ (AMDH)(AMD) ₂ (O ₂ CC ₄ F ₉) ₂] ⁺	1296	-	-	1	4	<1
[Cu ₂ (AMDH) ₂ (O ₂ CC ₄ F ₉) ₃] ⁺	1239	6	38	35	5	1
[Cu ₂ (AMDH)(O ₂ CC ₄ F ₉) ₃] ⁺	1077	2	8	33	23	2
[Cu ₃ (NH ₂)(O ₂ CC ₄ F ₉) ₃] ⁺	996	2	<1	2	4	2
[Cu ₃ (O ₂ CC ₄ F ₉) ₃] ⁺	980	-	<1	1	4	3
[Cu ₂ (AMDH)(AMD)(O ₂ CC ₄ F ₉) ₂] ⁺	975	<1	2	3	1	<1
[Cu ₂ (O ₂ CC ₄ F ₉) ₃] ⁺	915	-	<1	1	2	4
[Cu ₃ (NH ₂)(AMD)(O ₂ CC ₄ F ₉) ₂] ⁺	894	-	<1	2	5	3
[Cu ₃ (NH ₂)(AMD) ₂ (O ₂ CC ₄ F ₉) ₂] ⁺	792	-	<1	1	4	1
[Cu ₃ (O ₂ CC ₄ F ₉) ₂] ⁺	717	-	<1	1	6	5
[Cu ₂ (AMD) ₂ (O ₂ CC ₄ F ₉) - H] ⁺	710	1	7	9	7	1
[Cu ₂ (O ₂ CC ₄ F ₉) ₂] ⁺	652	3	23	35	43	53
[Cu(AMDH) ₂ (O ₂ CC ₄ F ₉)] ⁺	650	6	47	49	7	<1
[Cu ₂ (AMDH)(O ₂ CC ₄ F ₉)] ⁺	551	1	10	21	23	7
[Cu ₂ (AMD)(O ₂ CC ₄ F ₉)] ⁺	550	1	7	26	84	44
[Cu(AMDH)(HN=C=NH)(O ₂ CC ₄ F ₉)] ⁺	530	<1	4	4	1	<1
[Cu(AMDH)(O ₂ CC ₄ F ₉)] ⁺	488	1	8	27	23	2
[Cu ₂ (AMD) ₂] ⁺	448	1	4	7	17	7
[Cu ₂ (O ₂ C)(O ₂ CC ₄ F ₉)] ⁺	433	<1	1	3	9	7
[Cu ₂ (O ₂ CC ₄ F ₉)] ⁺	389	1	21	75	1	1
[Cu ₂ (AMD)] ⁺	287	1	9	29	68	43
[Cu(AMDH)(HN=C=NH)] ⁺	267	4	21	13	4	1
[Cu(AMD)(HCN)] ⁺	251	<1	1	1	3	70
[Cu(AMDH)] ⁺	225	6	54	99	57	7
[C ₄ F ₉] ⁺	219	2	16	52	100	100
[AMDH] ⁺	162	5	23	43	31	14
[Cu ₂ F] ⁺	145	<1	3	18	34	41
[C ₂ F ₄ CN] ⁺	126	1	1	2	4	6
[C ₂ F ₅] ⁺	119	100	1	1	1	2
[C ₂ F ₄] ⁺	100	81	1	2	3	4
[CF ₂ CN] ⁺	76	1	1	1	1	1
[CF ₂] ⁺	50	69	88	100	75	89
[CO ₂ H] ⁺	45	16	67	1	1	1
[CO ₂] ⁺	44	3	3	3	2	3
[HN=C-NH ₂] ⁺	43	35	100	1	84	24
[HN=C=NH] ⁺	42	15	16	19	9	4
[F ₂] ⁺	38	59	29	10	4	4

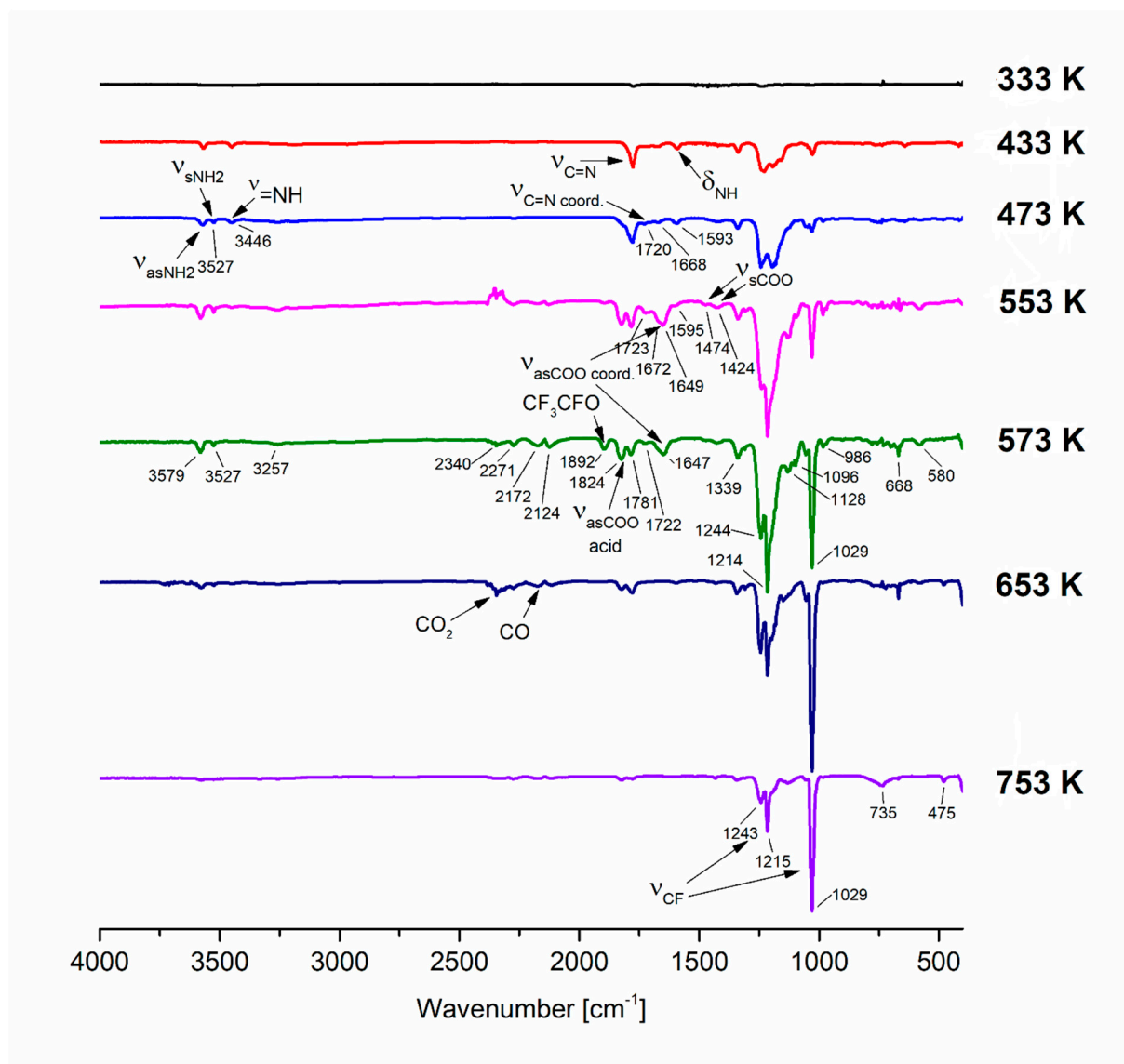


Figure S5. VT IR spectra of $[\text{Cu}_2(\text{AMDH})_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (1) in the temperature range 333–753 K.

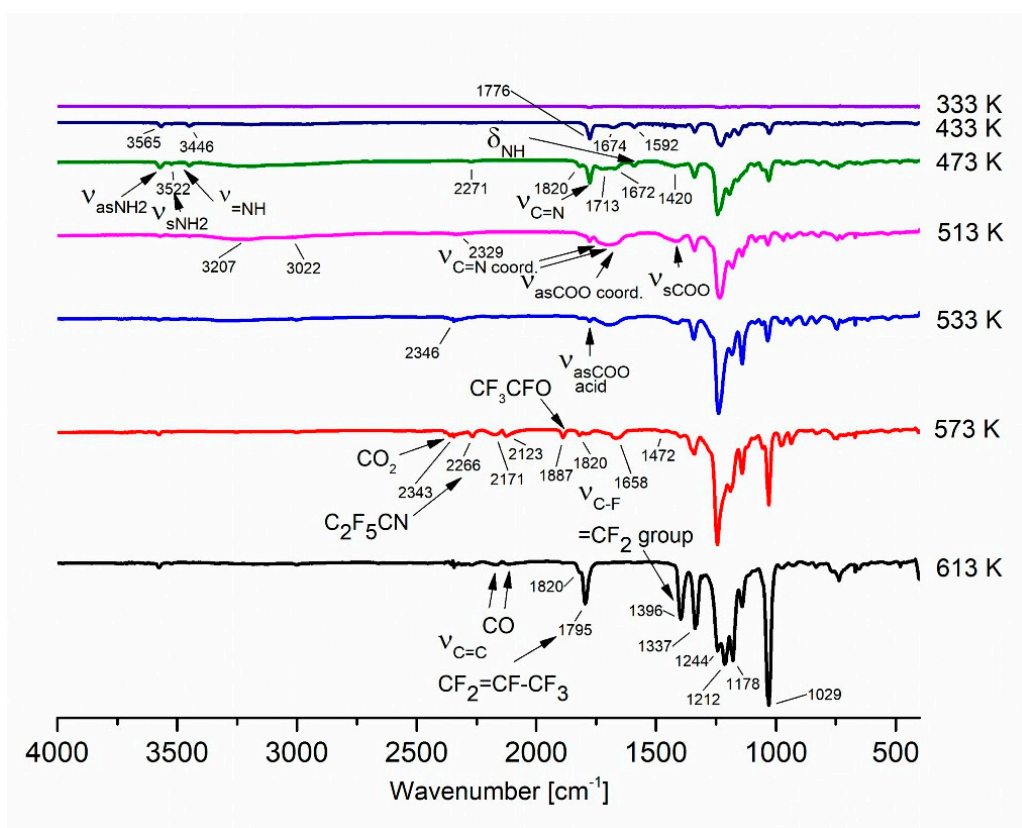


Figure S6. VT IR spectra of $[\text{Cu}_2(\text{AMDH})_2(\mu\text{-O}_2\text{CC}_3\text{F}_7)_4]$ (3) in the temperature range 333–613 K.

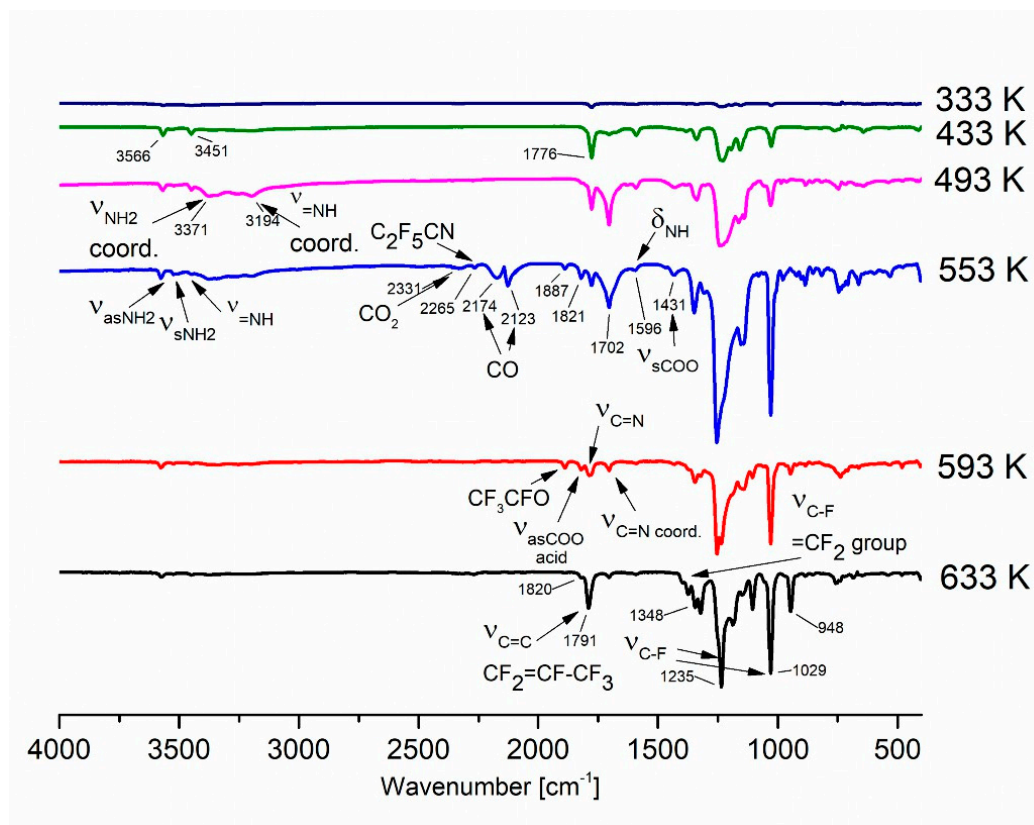


Figure S7. VT IR spectra of $[\text{Cu}_2(\text{AMDH})_2(\mu\text{-O}_2\text{CC}_4\text{F}_9)_4]$ (4) in the temperature range 333–633 K.

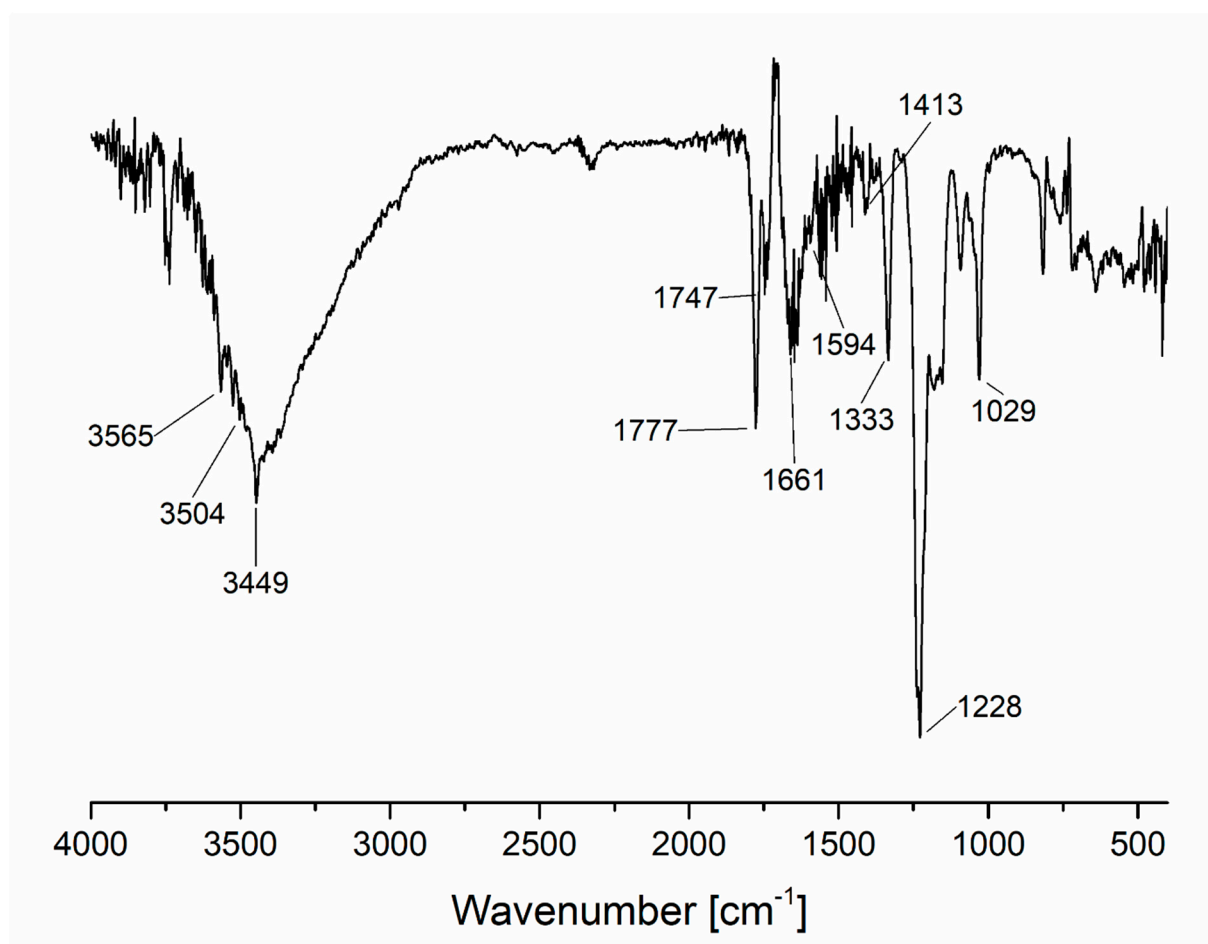


Figure S8. IR spectrum in the gas phase at 353 K for the complex $[\text{Cu}_2(\text{AMDH})_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (2).