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The Crystal and Molecular Structure of Copper(II) Formate Monourea

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The crystal and molecular structure of copper(II) formate monourea has been determined by a single-crystal X-ray structural analysis. This material forms green crystals with triclinic symmetry, space group $P\bar{1}$, a = 6.677 (13) Å, b = 6.822 (14) Å, c = 9.093 (18) Å, α = 76° 44′ (10′), β = 116° 20′ (10′), and γ = 113° 0′ (10′). Observed and calculated (Z = 2) densities are 2.10 (2) and 2.08 g/cm^3, respectively. The structural determination was based upon 616 independent film data and a full-matrix least-squares refinement which converged to a conventional R factor of 0.089. The crystal structure is comprised of centrosymmetric dimers, $[Cu(O_2CH)_2OC(NH_2)_2]_2$, packed in a manner such that alternate layers of urea and $Cu_2(O_2CH)_4$ moieties are approximately perpendicular to the c axis. Intra- and intermolecular hydrogen bonds are probably present. The two metal atoms in the dimer are linked by four bridging formate ions. The monodentate urea molecules are probably O bonded to the copper atoms. The Cu–Cu and mean Cu–O(formate) distances are 2.657 (7) and 1.952 (13) Å, respectively.

Introduction

Considerable speculation has centered upon the nature of the metal–metal interaction in dimeric copper(II) carboxylates. Pertinent aspects of this problem have been discussed in several recent reviews.[1–5] It was early established that the anomalous magnetic properties of anhydrous copper(II) *n*-alkanoates and their monoadducts ($\mu_{eff} \approx 1.4$ BM, $|2J| \approx 280$ cm^{-1}, $T_c \approx 255$°K)[6] could be interpreted in terms of exchange coupling between magnetically isolated pairs of copper(II) ions. Structural studies have shown that a number of the copper(II) complexes are in fact *syn–syn*[7,8] carboxylate-bridged dimers with two copper atoms 2.6–2.7 Å apart.[9–18] With this solid-state configuration well documented, discussion now centers upon the mechanism of exchange coupling within the dimeric unit. Direct Cu–Cu interaction[3,19] and superexchange *via* the bridging carboxylate groups[20,21] are the two models which have been most frequently advanced.

The different tendencies for dimer formation by the copper(II) formate and *n*-alkanoate derivatives have been a related matter of interest. In particular, the contrasting structures of dimeric cupric acetate monohydrate[9,12] and of polymeric cupric formate tetrahydrate[22,23] prompted Martin and Waterman to investigate these systems extensively and to suggest a plausible explanation for this difference. They interpreted the relative dissociation constants of formic and acetic acids to reflect the greater σ-electron density on the hydroxyl oxygen of the latter compound and concluded that the resultant lesser residual charge on the copper atom could be the predominant factor causing the dimeric structure in cupric acetate monohydrate.[8] These workers were subsequently able to prepare copper(II) formate monoamine and hemidioxane adducts. It was suggested on the basis of the anomalous magnetic properties of these compounds that their more basic addends favored dimer formation in cupric formate by reducing the residual charge on the copper dication. The magnetic properties of these presumably dimeric copper(II) formate adducts ($\mu_{eff} \approx 1.0$ BM, $|2J| > 408$ cm^{-1}, $T_c \approx 500$°K) were considered to reflect an even stronger direct metal–metal interaction than that proposed for the related *n*-alkanoate complexes. The greater energy of the singlet–triplet separation in the copper(II) formate dimers with respect to that of the *n*-alkanoate dimers was attributed to increased $3d_\delta$–$3d_\delta$ overlap induced by the formate anions.[24]

Only a very limited amount of detailed structural data is available for dimeric cupric formate monoadduct complexes. A two-dimensional X-ray structural determination of cupric formate hemidioxane has confirmed that in this adduct pairs of copper ions are

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(6) μ_{eff} is the effective room-temperature magnetic moment, $|2J|$ is the exchange coupling constant for the magnetic interaction, and T_c is the Néel temperature.

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syn–syn bridged by four formate groups. The $Cu_2(O_2CH)_4$ units form infinite chains along the copper–copper direction with bidentate dioxane molecules bridging axial sites of adjacent metal couples.[16] A recent report of the structure of the compound $[(CH_3)_4N]_2[Cu_2(O_2CH)_4(NCS)_2]$ has provided another example of a dimeric copper(II) formate adduct. The structure of the analogous acetate anion was also reported; comparison of these two structures showed that the formate derivative had the longer Cu–Cu distance (2.716 (2) *vs* 2.643 (3) Å for the acetate) in spite of its greater magnetic exchange coupling ($|2J|$ = 485 cm^{-1} *vs.* 305 cm^{-1} for the acetate). Goodgame, *et al.*, considered these results to demonstrate that the contribution of a direct metal–metal interaction to the magnetic exchange interaction in copper(II) carboxylate dimers is insignificant.[18]

In the course of their studies of urea adducts of a series of copper(II) alkanoates, Kishita, *et al.*, showed that cupric formate forms a monourea adduct with a very low room-temperature magnetic moment of 1.08 BM. Although temperature-dependent magnetic susceptibility measurements were not reported, this result strongly suggests that dimer formation is also favored by the urea addend.[25] The present structural studies on this compound were undertaken to obtain reliable structural parameters on a possible copper(II) formate dimer as part of an attempt to ascertain whether any structural variations can be correlated with the appreciable differences in magnetic properties observed for the assorted adducts of copper(II) formate and *n*-alkanoates.

On the basis of infrared measurements and assignments there has been some speculation as to the nature of the copper–urea interaction in copper(II) formate monourea and other cupric alkanoate monourea compounds.[26] Since there are few documented structures of urea coordination compounds,[27–31] the urea configuration in the present structure was of interest also.

Experimental Section

Copper(II) formate diurea dihydrate was prepared as previously described.[25] Trituration of this compound in several small portions of methanol gave copper(II) formate monourea as a fine green powder. Crystals of this latter compound were obtained from a methanol solution by slow evaporation with a water aspirator. Difficulty was encountered in finding untwinned crystals. Examination of several suitable crystals by precession and Weissenberg X-ray photographic methods suggested their triclinic symmetry and revealed no systematic absences in their reflection data.

Lattice constants at 23° were determined from zero-level precession photographs which were calibrated by superposition of a single-crystal zero-level sodium chloride (*a* = 5.6405 Å) exposure. Zirconium-filtered Mo Kα radiation (λ 0.71069 Å) was used throughout the structural analysis. The direct lattice constants with standard deviations estimated by past experience with the above calibration technique are *a* = 6.677 (13) Å, *b* = 6.822 (14) Å, *c* = 9.093 (18) Å, α = 76° 44′ (10′), β = 116° 20′ (10′), and γ = 113° 0′ (10′). Delaunay reduction of this cell failed to reveal higher symmetry. The three shortest noncoplanar lattice translations defined a cell with *a* = 6.677 Å, *b* = 6.822 Å, *c* = 8.567 Å, α = 86° 31′, β = 107° 58′, and γ = 113° 0′. The transformation matrix to the reduced cell is $(\bar{1}00/0\bar{1}0/101)$; all results are reported in terms of the nonreduced cell. The density of the compound, 2.10 (2) g/cm^3, was determined by flotation in a CH_2Br_2–C_6H_5Br mixture and agrees well with the density d_c = 2.08 g/cm^3 calculated for two monomer units per cell. Of the two possible triclinic space groups, the centrosymmetric space group $P\bar{1}$ was assumed on the basis of its more frequent occurrence. Successful solution and refinement in this space group support this choice.

Multiple-film equiinclination Weissenberg intensity data were collected from a tabular crystal approximately 0.23 mm × 0.12 mm × 0.06 mm mounted in a Lindemann capillary roughly parallel to its long dimension and its *b* axis. A standard set of intensities was prepared from the same crystal. This intensity scale was used for visual estimation of the 616 independent, nonzero reflections on the top and bottom halves of films for the levels *h*0*l* through *h*5*l*. Preliminary and final zero-level photographs indicated that some crystal deterioration (as evidenced by a slight broadening of the spots) had taken place over the period of data collection.

The intensity data from the top halves of the films were corrected for Lorentz and polarization effects and for spot extension; only Lorentz and polarization corrections were applied to those from the bottom halves of the film. An absorption correction was omitted since it was estimated that the maximum effect of absorption on the intensities within a given layer was approximately 15%.

Solution and Refinement of the Structure

An assumed intramolecular copper–copper vector of length ~2.6 Å was readily identified on the three-dimensional Patterson map. The vector distribution was consistent with the assumed centrosymmetric space group. Full-matrix least-squares refinement of the copper atomic coordinates, an isotropic temperature factor, and 11 scale factors yielded discrepancy factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.341$ and $R_2 = [\Sigma w \cdot (|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.399$. The remaining 10 nonhydrogen atoms of the asymmetric unit were located from a difference Fourier map phased on the copper atom contributions to F_c. As it is chemically reasonable for either the oxygen or the nitrogen of a unidentate urea to coordinate to copper, the oxygen and two nitrogens of the addend were all treated as nitrogen atoms in the initial stages of refinement. Three cycles of least-squares refinement of the 11 scale factors, all atomic coordinates, and isotropic temperature factors reduced the discrepancy factors to $R_1 = 0.145$ and $R_2 = 0.167$. Up to this point, unit weights were used in all refinements. At this stage several errors in the data were corrected and the weights were adjusted to eliminate any systematic dependence of mean $\Delta F/\sigma$ values upon observed *F*, uncorrected intensity, and Bragg angle. This was accomplished with the weighting scheme: $\sigma(F_o) =$

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1.0 for $F_o < 9.1F_{\min}$, $\sigma(F_o) = F_o/9.1F_{\min}$ for $F_o \geqslant 9.1F_{\min}$. Here $F_{\min}$ is the minmum observed F for the entire data set. Only the 33 largest structure amplitudes were given nonunit weights by this procedure; the criteria upon which the choice of weights was based were fulfilled throughout the remainder of the refinement. Comparison of partial R factors and mean $\Delta F/\sigma$ values revealed no differences between data observed on the top and bottom halves of the films. This suggests that the treatment of the data from the lower halves of the films was adequate.

Two additional cycles of isotropic least-squares refinement reduced the discrepancy factors to $R_1 = 0.124$ and $R_2 = 0.139$. Further refinement with anisotropic temperature factors assigned to the copper atom converged to R_1 and R_2 values of 0.089 and 0.104, respectively. An attempt was now made to resolve which of three possible unidentate urea arrangements exists in the present compound. Based on the previous least-squares output, two further cycles of refinement were carried out for each of the models with isotropic thermal parameters for the oxygen and the two nitrogens of the urea ligand. Refined individual positional parameters for the three models differed by less than 0.5 standard deviation. However considerable variation occurred in the isotropic thermal parameters obtained from the three refinements. These data are summarized with other relevant information in Table I. For the O-coordinated urea (model 3), all three atoms have reasonable thermal parameters considering their environment and the thermal parameters of the other light atoms in the structure (Table II). By the same criteria the nitrogen-coordinated alternatives (models 1 and 2) have low thermal parameters for their atoms coordinated to the copper atom and high thermal parameters for their oxygen atoms at the next furthest [A(2)] and furthest [A(3)] sites, respectively, from the metal. Collectively these trends for the three refined urea configurations lead us to consider the O-coordinated urea as the most reasonable model for cupric formate monourea. However it must be emphasized that the accuracy of the present X-ray structural determination is insufficient to support an unequivocal distinction of O- *vs.* N-coordinated urea solely on the basis of the observed variations in isotropic thermal parameters. Some structural features relevant to the assignment of the urea model are presented in the Discussion. In line with our preference for an O-bonded urea, all tabulated data are derived from the final cycle of least-squares refinement on model 3 in which no parameter shifted by more than 0.4 standard deviation. The final standard deviation of an observation of unit weight was 0.76.

TABLE I

SELECTED RESULTS OF REFINEMENT FOR THE THREE UREA COORDINATION MODELS[a]

	Model			
Parameter	Initial A(1), A(2), A(3) = N	1 A(2) = O	2 A(3) = O	3 A(1) = O
B(A(1))	2.1 (3)	2.1 (3)	2.1 (3)	3.6 (3)
B(A(2))	3.5 (4)	5.3 (4)	3.4 (4)	3.5 (4)
B(A(3))	4.3 (4)	4.2 (4)	6.2 (4)	4.2 (4)
R_1	0.089	0.088	0.090	0.089
R_2	0.104	0.104	0.105	0.105

[a] Using these generalized labels A(1) refers to the urea atom coordinated to the copper while A(2) and A(3) refer, respectively, to the urea atoms next furthest and furthest away from the copper. B(A(1)) denotes the isotropic thermal parameter of atom A(1), etc.

TABLE II

ATOMIC POSITIONAL AND THERMAL PARAMETERS FOR $[Cu(O_2CH)_2OC(NH_2)_2]_2$[a]

Atom	x	y	z	B, Å^2
Cu	−0.0238 (5)	−0.0994 (4)	0.1381 (3)	*b*
O(1)	0.2812 (24)	0.1055 (25)	0.2541 (16)	4.0 (3)
O(2)	0.1378 (23)	−0.2720 (24)	0.1220 (15)	3.4 (3)
O(3)	−0.3225 (24)	−0.2718 (24)	−0.0222 (16)	4.0 (3)
O(4)	−0.1784 (25)	0.1072 (25)	0.1084 (16)	3.8 (3)
O(5)	−0.0824 (23)	−0.2869 (23)	0.3444 (15)	3.6 (3)
N(1)	−0.2882 (28)	−0.1359 (29)	0.3968 (19)	3.5 (4)
N(2)	−0.1891 (30)	−0.4156 (31)	0.5618 (21)	4.2 (4)
C(1)	0.3994 (35)	0.2549 (36)	0.1763 (24)	3.6 (4)
C(2)	0.2089 (34)	−0.2473 (35)	0.0070 (23)	3.3 (4)
C(3)	−0.1812 (31)	−0.2731 (32)	0.4339 (20)	2.5 (3)

[a] Numbers in parentheses in all tables and in the text are estimated standard deviations in the least significant figures. [b] An isotropic thermal ellipsoid of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ was assigned to the copper atom. The final thermal parameters β_{ij} are 0.0314 (9), 0.0151 (24), 0.0108 (4), 0.0104 (8), 0.0127 (5), and 0.036 (4), respectively.

A final difference Fourier map was calculated on which the maximum peak height was 1.3 e$^-$/Å^3. This may be compared with a peak height range 2.1–5.3 e$^-$/Å^3 observed for the carbon, nitrogen, and oxygen atoms on the previous difference map. No convincing evidence of the effects of hydrogen atoms was found on this map.

The least-squares program UCILS2, a local version of the Busing–Martin–Levy program ORFLS, was employed throughout the refinement. The scattering factor tables compiled by Ibers were used for Cu, O, N, and C.[32] The correction for anomalous scattering by Cu incorporated the $\Delta f'$ and $\Delta f''$ values of Cromer.[33] The final values of observed and calculated structure factors are listed in Table III. Unobserved data were not included in the refinement; however structure factors up to the limiting value of θ were calculated for the unobserved reflections. These revealed no significant discrepancies within the experimentally accessible region of reciprocal space.

The final atomic positional and thermal parameters for the O-coordinated urea model of copper(II) formate monourea are presented in Table II. The principal root-mean-square amplitudes of thermal motion for the copper atom are 0.141 (4), 0.167 (14), and 0.236 (4) Å.[34] Interatomic distances and angles are tabulated in Tables IV and V. These values and their

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[34] The axis of minimum rms amplitude is roughly (within 10°) parallel to the Cu–Cu vector. Maximum thermal motion occurs approximately in the O(1)–O(3) direction.

TABLE III

FINAL VALUES OF OBSERVED AND CALCULATED STRUCTURE FACTORS IN ELECTRONS (×10)

H	L	FO	FC
* * * K = 0 * * *			
0	-2	110	103
0	-3	286	312
0	-4	443	439
0	-6	110	95
0	-7	240	267
0	-8	143	150
1	0	749	702
1	1	225	212
1	2	117	136
1	3	141	140
1	4	426	406
1	5	235	265
1	7	119	107
1	-1	309	275
1	-2	128	120
1	-3	645	580
1	-4	620	522
1	-6	145	158
1	-7	255	273
1	-8	134	173
2	0	74	26
2	1	418	407
2	2	59	75
2	3	226	231
2	4	241	231
2	5	127	148
2	-2	425	384
2	-3	432	421
2	-4	540	482
2	-6	236	268
2	-7	84	106
2	-8	84	89
2	-9	51	71
2	-10	107	123
3	0	212	195
3	1	273	279
3	3	104	84
3	-1	64	64
3	-2	167	185
3	-3	108	124
3	-4	201	216
3	-5	72	75
3	-6	256	265
3	-7	136	168
3	-8	126	136
3	-9	189	179
3	-10	140	146
4	0	160	139
4	1	144	154
4	4	96	65
4	5	105	78
4	-2	99	96
4	-3	238	257
4	-5	202	200
4	-6	122	149
4	-7	151	187
4	-8	87	81
4	-9	93	102
4	-10	99	120
5	0	124	105
5	1	141	136
5	-2	117	98
5	-3	294	313
5	-4	118	115
5	-5	116	124
5	-6	160	180
5	-7	175	191
5	-10	117	133
6	0	93	77
6	1	103	95
4	2	100	89
6	-2	103	82
6	-3	107	134
6	-6	136	148
6	-7	196	183
* * * K = 1 * * *			
0	2	183	177
0	4	333	347
0	5	374	378
0	6	95	104
0	7	104	83
0	8	148	154
0	-1	88	115
0	-2	234	225
0	-3	585	583
0	-4	221	229
0	-5	133	146
0	-6	183	190
0	-7	182	190
0	-8	106	98
1	1	1037	996
1	2	254	270
1	4	310	329
1	5	361	368
1	7	96	83
1	8	114	133
1	-1	121	119
1	-2	380	391
1	-3	914	811
1	-4	243	229
1	-5	74	57
1	-6	325	307
1	-7	139	156
1	-8	96	75
2	0	303	314
2	1	627	681
2	2	351	376
2	3	92	104
2	4	117	103
2	5	124	112
2	-1	83	87
2	-2	301	340
2	-3	467	444
2	-4	160	182
2	-5	165	151
2	-6	394	390
2	-7	268	258
2	-9	155	148
3	0	165	166
3	1	116	107
3	2	157	161
3	4	92	70
3	5	108	93
3	6	105	99
3	-1	172	192
3	-2	279	283
3	-3	235	245
3	-5	229	234
3	-6	128	147
3	-7	269	246
3	-9	153	143
3	-10	110	109
4	2	100	73
4	-1	144	130
4	-2	242	244
4	-3	260	280
4	-5	185	201
4	-6	187	163
4	-9	139	142
4	-10	112	116
5	1	99	67
5	2	109	88
5	-2	92	98
5	-5	103	104
5	-6	177	189
5	-8	144	119
5	-9	117	133
6	-2	109	112
6	-4	102	88
6	-5	103	98
6	-6	159	158
7	-2	114	95
-1	0	872	680
-1	2	227	170
-1	3	529	394
-1	4	248	242
-1	5	182	168
-1	7	173	221
-1	8	105	124
-1	9	99	79
-1	-1	258	259
-1	-2	308	269
-1	-3	128	146
-1	-4	224	210
-1	-5	106	132
-1	-6	129	121
-1	-7	145	111
-2	0	52	66
-2	1	49	55
-2	2	104	67
-2	3	364	344
-2	4	258	260
-2	5	260	232
-2	6	161	137
-2	7	197	212
-2	9	136	105
-2	10	104	104
-2	-1	176	211
-2	-2	75	86
-2	-3	193	186
-2	-4	224	241
-2	-6	92	82
-2	-7	100	77
-3	0	407	405
-3	1	131	124
-3	2	166	167
-3	3	120	120
-3	4	400	383
-3	5	200	185
-3	6	215	198
-3	7	189	196
-3	8	94	117
-3	10	155	127
-3	-1	125	130
-3	-3	177	205
-3	-4	129	127
-3	-7	107	77
-4	0	404	425
-4	1	280	305
-4	3	77	84
-4	4	314	319
-4	6	142	156
-4	7	241	250
-4	8	292	284
-4	-1	175	168
-5	0	153	165
-5	1	122	142
-5	3	235	271
-5	4	276	294
-5	6	125	142
-5	7	153	166
-5	8	210	194
-5	-1	171	160
-6	3	196	205
-6	4	214	259
-6	5	92	81
-6	6	114	119
-6	7	118	144
-6	8	111	92
-7	7	116	130
* * * K = 2 * * *			
0	0	316	320
0	1	68	89
0	4	262	255
0	5	296	301
0	6	177	176
0	-1	257	265
0	-2	367	379
0	-3	506	466
0	-4	149	128
0	-5	123	137
1	1	374	386
1	2	612	645
1	5	175	175
1	-1	119	108
1	-2	483	470
1	-3	309	290
1	-5	288	259
1	-6	263	257
1	-8	195	150
1	-9	152	138
2	0	169	176
2	1	225	229
2	2	442	507
2	6	140	152
2	-1	242	235
2	-2	450	461
2	-5	328	309
2	-6	302	282
2	-7	222	191
2	-9	161	139
3	1	115	129
3	2	198	204
3	3	140	142
3	-1	288	308
3	-2	416	438
3	-3	174	185
3	-4	122	143
3	-5	274	268
3	-6	203	189
3	-9	153	122
4	-1	132	99
4	-2	177	178
4	-3	132	125
4	-4	134	130
4	-5	138	150
4	-6	224	214
4	-8	163	150
-1	0	122	107
-1	2	134	132
-1	3	86	90
-1	4	228	235
-1	5	125	107
-1	6	212	196
-1	8	129	141
-1	-1	76	94
-1	-2	224	255
-1	-3	225	234
-1	-4	160	133
-1	-5	175	165
-1	-6	178	184
-2	0	100	103
-2	1	734	797
-2	2	529	563
-2	3	92	79
-2	4	184	157
-2	5	216	182
-2	7	227	203
-2	8	207	186
-2	9	124	127
-2	-2	184	190
-2	-3	163	161
-2	-5	110	111
-2	-6	139	167
-3	0	179	179
-3	1	390	414
-3	2	265	280
-3	3	102	94
-3	4	254	240
-3	5	564	485
-3	7	165	170
-3	8	180	168
-3	9	195	182
-3	-2	144	155
-3	-3	284	331
-3	-4	134	164
-4	0	365	412
-4	1	325	332
-4	2	127	136
-4	3	189	183
-4	4	360	356
-4	5	504	455
-4	6	121	129
-4	7	188	174
-4	8	194	186
-4	9	132	127
-4	-2	156	159
-4	-3	188	211
-5	0	184	204
-5	1	233	237
-5	2	101	107
-5	3	110	127
-5	4	235	233
-5	5	230	233
-5	7	173	162
-5	8	186	200
-5	9	151	149
-6	1	119	121
-6	3	114	85
* * * K = 3 * * *			
0	0	127	95
0	2	401	387
0	3	195	165
0	5	163	195
0	-1	146	158
0	-2	319	315
0	-4	178	178
0	-5	289	265
0	-6	104	100
0	-8	147	154
1	0	127	122
1	2	194	217
1	3	86	72
1	6	115	88
1	-1	203	201
1	-2	199	198
1	-3	197	160
1	-4	134	131
1	-5	195	201
1	-6	159	159
1	-7	111	72
1	-8	145	157
2	0	147	125
2	1	87	15
2	2	52	86
2	3	171	197
2	6	126	127
2	-1	433	455
2	-2	240	244
2	-4	203	199
2	-5	160	159
2	-7	167	115
2	-8	139	144
2	-9	128	108
3	0	97	71
3	2	104	85
3	3	176	226
3	-1	220	253
3	-2	146	142
3	-4	231	242
3	-5	235	229
3	-6	117	108
3	-7	116	107
3	-8	148	152
4	0	117	121
4	2	117	100
4	3	122	109
4	-1	115	125
4	-2	107	45
4	-4	169	160
4	-5	202	196
4	-6	117	107
5	-1	122	124
5	-5	122	130
-1	0	45	43
-1	2	272	341
-1	3	211	217
-1	5	205	200
-1	6	246	228
-1	8	96	126
-1	9	105	95
-1	-1	316	322
-1	-2	429	417
-1	-3	67	85
-1	-4	118	123
-1	-5	187	210
-1	-6	93	103
-2	0	149	140
-2	1	476	503
-2	2	540	630
-2	3	137	148
-2	4	136	171
-2	5	142	138
-2	6	332	317
-2	7	84	72
-2	8	132	113
-2	9	110	116
-2	-1	243	249
-2	-2	418	410
-2	-3	133	142
-2	-4	87	108
-2	-5	146	156
-2	-6	187	201
-3	0	129	112
-3	1	590	512
-3	2	427	585
-3	3	305	287
-3	4	243	234
-3	5	374	325
-3	6	331	299
-3	8	160	158
-3	9	168	168
-3	10	123	126
-3	-1	146	156
-3	-2	275	280
-3	-3	222	247
-3	-6	113	124
-4	1	202	210
-4	2	143	147
-4	3	67	66
-4	4	260	231
-4	5	384	364
-4	6	324	292
-4	8	158	148
-4	10	123	88
-4	-1	120	115
-4	-2	193	202
-4	-3	210	228
-5	0	117	99
-5	1	176	176
-5	2	179	192
-5	3	78	83
-5	4	122	106
-5	5	227	225
-5	6	189	175
-5	7	104	86
-5	8	158	154
-5	-2	103	104
-6	1	114	122
-6	2	145	157
-6	5	123	123
-6	7	141	118
-6	8	101	127
-6	9	168	165
-7	1	106	91
-7	4	101	97
-7	5	117	137
* * * K = 4 * * *			
0	0	194	182
0	1	100	100
0	2	193	202
0	3	298	324
0	4	100	104
0	-1	245	233
0	-3	106	88
0	-4	290	269
0	-5	249	232
0	-6	129	120
1	0	203	213
1	3	105	117
1	-1	298	312
1	-3	164	160
1	-4	191	195
1	-5	110	100
2	0	150	124
2	3	111	79
2	-1	176	208
2	-4	176	181
2	-5	114	102
2	-6	132	116
2	-7	189	166
2	-8	136	122
3	0	179	161
3	3	124	64
3	-1	111	36
3	-3	113	108
3	-4	134	144
4	0	145	151
4	-3	136	131
4	-4	126	118
-1	0	195	201
-1	2	292	307
-1	3	483	531
-1	4	181	183
-1	5	136	149
-1	6	152	137
-1	7	112	124
-1	-1	464	441
-1	-2	282	275
-1	-4	220	206
-1	-5	240	232
-2	0	146	170
-2	3	211	262
-2	4	131	123
-2	5	160	189
-2	6	271	289
-2	7	230	278
-2	-1	476	461
-2	-2	395	387
-2	-5	165	166
-3	0	147	132
-3	1	123	119
-3	2	464	448
-3	3	178	194
-3	5	200	208
-3	6	184	203
-3	7	195	189
-3	9	110	112
-3	-1	234	233
-3	-2	235	233
-3	-5	115	121
-4	0	103	89
-4	2	221	232
-4	3	322	317
-4	5	162	139
-4	6	176	164
-4	8	115	109
-4	9	148	138
-4	-1	118	104
-4	-4	105	110
-5	2	89	89
-5	3	127	131
-5	4	124	113
-5	6	203	204
-5	8	153	130
-5	-1	101	110
-6	1	104	97
-6	2	213	198
-6	6	206	181
-6	8	114	105
-6	9	133	130
-7	1	159	73
-7	2	154	140
-7	5	157	153
-7	6	106	102
-7	9	124	132
-8	5	166	146
* * * K = 5 * * *			
0	0	379	379
0	1	178	171
0	3	152	143
0	4	203	199
0	5	113	55
0	-1	188	197
0	-3	175	159
0	-4	235	192
0	-5	128	82
1	0	218	222
1	1	101	83
1	3	117	81
1	4	169	146
1	-1	110	126
1	-3	222	226
1	-4	176	176
2	0	113	90
2	4	130	90
2	-3	184	150
2	-4	176	145
3	0	135	109
3	1	137	98
-1	0	262	287
-1	3	265	306
-1	4	188	205
-1	6	112	102
-1	-1	257	259
-1	-4	287	257
-1	-5	122	122
-2	0	203	218
-2	3	255	305
-2	4	181	196
-2	6	206	187
-2	7	126	125
-2	-1	292	318
-2	-4	128	157
-3	0	150	171
-3	1	54	50
-3	3	64	104
-3	4	91	136
-3	6	112	118
-3	7	122	153
-3	8	94	85
-3	-1	144	168
-3	-3	126	143
-4	0	144	150
-4	2	180	187
-4	3	204	223
-4	4	133	148
-4	5	136	143
-4	7	93	112
-4	9	110	101
-4	-1	76	74
-4	-3	105	117
-5	0	121	86
-5	2	113	88
-5	3	268	256
-5	4	138	110
-5	5	111	91
-5	6	114	123
-5	7	164	153
-5	9	106	98
-5	10	120	107
-5	-1	131	126
-6	2	136	110
-6	3	163	142
-6	6	239	221
-6	7	179	154
-6	-1	152	157
-7	2	150	142
-7	3	138	131
-7	6	198	173
-7	7	114	105

TABLE IV

INTRAMOLECULAR DISTANCES AND ANGLES

Distances, Å			
Cu···Cu′[a]	2.657 (7)	O(1)–C(1)	1.30 (2)
		O(2)–C(2)	1.28 (2)
Cu–O(1)	1.939 (16)	O(3)′–C(1)	1.26 (2)
Cu–O(2)	1.946 (14)	O(4)′–C(2)	1.25 (2)
Cu–O(3)	1.965 (16)		
Cu–O(4)	1.959 (16)		
		O(5)–C(3)	1.29 (2)
Cu–O(5)	2.114 (13)	N(1)–C(3)	1.29 (2)
		N(2)–C(3)	1.34 (2)
N(1)···O(5)	2.26 (2)		
N(2)···O(5)	2.27 (2)	O(4)···N(1)	2.99 (2)
N(1)···N(2)	2.26 (3)		
Angles, Deg			
Cu′···Cu–O(1)	86.8 (5)	Cu–O(1)–C(1)	121.9 (13)
Cu′···Cu–O(2)	83.9 (4)	Cu–O(2)–C(2)	124.8 (13)
Cu′···Cu–O(3)	80.7 (5)	Cu–O(3)–C(1)′	129.0 (14)
Cu′···Cu–O(4)	83.1 (4)	Cu–O(4)–C(2)′	125.9 (13)
Cu′···Cu–O(5)	174.0 (4)	Cu–O(5)–C(3)	132.4 (13)
O(1)–Cu–O(2)	89.4 (6)	O(1)–C(1)–O(3)′	121.6 (19)
O(1)–Cu–O(4)	89.9 (7)	O(2)–C(2)–O(4)′	122.3 (19)
O(2)–Cu–O(3)	89.6 (6)		
O(3)–Cu–O(4)	88.3 (6)		
		O(5)–C(3)–N(1)	121.9 (17)
		O(5)–C(3)–N(2)	119.2 (18)
O(1)–Cu–O(3)	167.5 (6)	N(1)–C(3)–N(2)	118.7 (16)
O(2)–Cu–O(4)	167.1 (5)		
		N(1)···O(4)–Cu	85.2 (6)
		N(1)···O(4)–C(2)	148.4 (13)
O(5)–Cu–O(1)	98.4 (6)		
O(5)–Cu–O(2)	93.1 (6)	C(3)–N(1)···O(4)	100.4 (11)
O(5)–Cu–O(3)	94.1 (6)		
O(5)–Cu–O(4)	99.8 (6)		

[a] Throughout this paper, primes refer to atoms related by the molecular center of symmetry to atoms in the asymmetric unit.

TABLE V

INTERMOLECULAR CONTACTS LESS THAN 3.4 Å

O(1)···N(1)′	$x, y, 1 + z$	3.21 (2)
O(1)···N(2)′	$x, y, 1 + z$	3.35 (2)
O(2)···N(2)′	$x, 1 - y, 1 + z$	3.13 (2)
O(2)···C(2)′	$x, 1 - y, z$	3.30 (3)
O(3)···C(2)	$1 - x, y, z$	3.33 (2)
O(5)···N(2)′	$x, 1 - y, 1 + z$	2.97 (3)
N(1)···N(1)′	$x, y, 1 + z$	3.37 (3)
N(1)···C(3)′	$x, y, 1 + z$	3.29 (3)

estimated standard deviations were computed with the Busing–Martin–Levy function and error program ORFFE; the standard deviations include the effects of interatomic correlations and estimated errors in the lattice constants. Least-squares planes were calculated with a modified version of D. L. Smith's program PLANET. Data concerning these planes are presented in Table VI. Other programs utilized during the course of this structure determination included a version of Zalkin's Fourier summation program FORDAP, and the plotting program DANFIG, by R. J. Dellaca and W. T. Robinson.

Discussion

The crystal structure of copper(II) formate monourea is composed of centrosymmetric dimers, $[Cu(O_2CH)_2OC(NH_2)_2]_2$. Four bidentate formate anions form *syn–syn* bridges between isolated pairs of copper atoms separated by 2.657 (7) Å. A diagram of the dimeric unit with pertinent intramolecular distances appears in Figure 1. The copper to formate oxygen distances range from 1.939 to 1.965 (16) Å. The copper to urea oxygen distance is 2.114 (13) Å. The metal atom is displaced 0.22 Å toward the urea ligand from the plane containing the four coordinated formate oxygen atoms. This molecular structure for copper(II) formate monourea is closely related to the reported structures of several other dimeric cupric carboxylate adducts, $Cu_2(O_2CR)_4L_2$: R = H, L = $^1/_2$(dioxane),[16] NCS^-;[18] R = CH_3, L = H_2O,[9,12]

TABLE VI

LEAST-SQUARES PLANES[a]

1. Plane Containing O(1), O(2), O(3), and O(4)

Equation of Plane:[b] $0.3723X + 0.4431Y - 0.8155Z = -1.1107$

Distances of atoms to plane, Å

O(1)	−0.004	O(5)	−2.325
O(2)	0.004	C(1)	1.171
O(3)	−0.004	C(1)′	1.050
O(4)	0.004	C(2)	1.132
Cu	−0.216	C(2)′	1.090
Cu′	2.437		

2. Plane Containing O(1), O(3), C(1), and Their Centrosymmetric Equivalents

Equation of Plane: $-0.7886X + 0.6145Y - 0.0221Z = 0.0000$

Distances of Atoms to Plane, Å

O(1)	−0.004	Cu	−0.006
O(3)	0.004	O(5)	−0.126
C(1)	0.005	N(2)	0.394

3. Plane Containing O(2), O(4), C(2), and Their Centrosymmetric Equivalents

Equation of Plane: $-0.5049X - 0.6783Y - 0.5338Z = 0.0000$

Distances of atoms to planes, Å

O(2)	0.002	Cu	0.000
O(4)	−0.002	O(5)	0.192
C(2)	−0.003	N(2)	0.345

4. Plane Containing O(5), N(1), N(2), and C(3)

Equation of Plane:

$-0.4556X - 0.6723Y - 0.5835Z = -0.0235$

Distances of Atoms to Plane, Å

O(5)	0.009	C(3)	−0.026
N(1)	0.009	O(2)	0.023
N(2)	0.008	O(4)	−0.112

Angles between Perpendiculars to Planes

Nos. of planes	Angle, deg	Nos. of planes	Angle, deg
1,4	89.5	2,4	92.3
2,3	90.4	3,4	4.0

[a] Unit weights were employed in the calculation of all planes. [b] The equations of the planes are expressed with respect to coordinates (X, Y, Z) referred to an orthogonal coordinate system (A, B, C) oriented with respect to the crystallographic axes (a, b, c) such that A is parallel to a and B lies in the (a, b) plane.

C_5H_5N (monoclinic[10] and orthorhombic[11] crystalline forms), NCS^-,[18] quinoline,[14] RCO_2^- = succinate, L = H_2O;[13] and RCO_2^- = acetylsalicylate, L = acetyl oxygen.[17] In addition some structural data for two related anhydrous compounds (R = C_2H_5 and n-C_3H_7) have been briefly reported.[15]

Apparent differences exist between the copper–copper and copper–apical oxygen distances found in the present study and those observed for cupric formate hemidioxane, the other neutral, dimeric copper(II) formate adduct for which X-ray structural data are available. However, the structural determination of the latter compound was based upon two-dimensional data and its precision is difficult to assess.[16] Hence we shall not discuss these differences further and shall employ our results in all comparisons.

The most notable point which emerges from a comparison of the molecular parameters of copper(II) formate monourea with those reported for other dimeric copper(II) carboxylates is the lack of any significant structural trends which may be related to the variations in magnetic properties of these compounds.

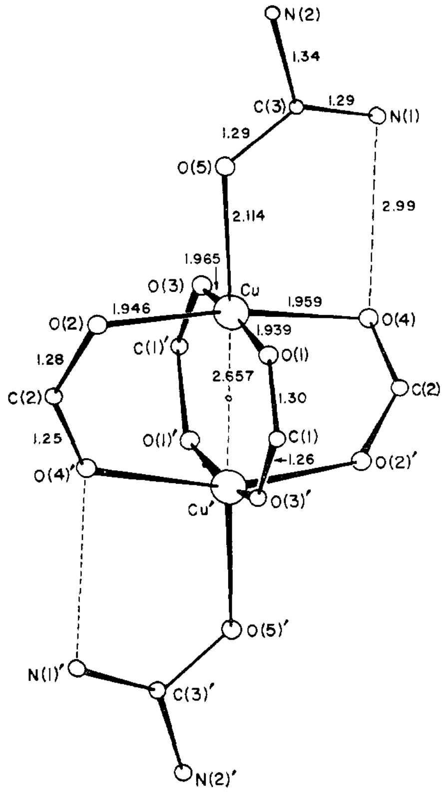

Figure 1.—Molecular structure of dimeric copper(II) formate monourea.

In particular, the Cu–Cu distance of 2.657 (7) Å in the urea adduct is 0.043 Å longer than the value of 2.614 Å reported for cupric acetate monohydrate,[12] even though the exchange coupling is greater in the former compound.[35] A similar observation was made by Goodgame, *et al.* (*vide supra*), for $[(CH_3)_4N]_2$-$[Cu_2(O_2CR)_4(NCS)_2]$, R = H, CH_3. As these workers pointed out, there is at present no simple reconciliation of the longer Cu–Cu separation and the greater exchange coupling in the formate adducts with the view that a direct metal–metal interaction is present in these dimers.[18] Thus the reason for the longer Cu–Cu distance in the formate dimers together with the mechanism of exchange coupling remains uncertain.

It was noted by Goodgame, *et al.*, that in spite of the long Cu–Cu distance in the anionic formate complex, the path length *via* the bridging ligand (*i.e.*, the total Cu–O–C–O–Cu distance) was shorter in the formate than in the acetate derivative.[18] Though we cannot make as direct a comparison as theirs, it is of some interest that the mean bridging path length of 6.45 Å for the present compound is the same as the corresponding distance of 6.45 Å found in hydrated cupric acetate. In fact, this distance is virtually identical (6.44 ± 0.02 Å) for all dimeric cupric carboxylates with the lone exception of $Cu_2(O_2CCH_3)_4(NCS)_2^{2-}$ (6.54 Å). The difference of 0.10 Å for this compound is primarily due to its Cu–O bond length of 2.03 (1) Å, about

(35) Temperature-dependent magnetic susceptibility investigations have not been reported for copper(II) formate monourea. However the low room-temperature magnetic moment[25] and the structure suggest that exchange coupling would be of the order observed for other dimeric copper(II) formate adducts,[8] $|2J| > 480$ cm^{-1}.

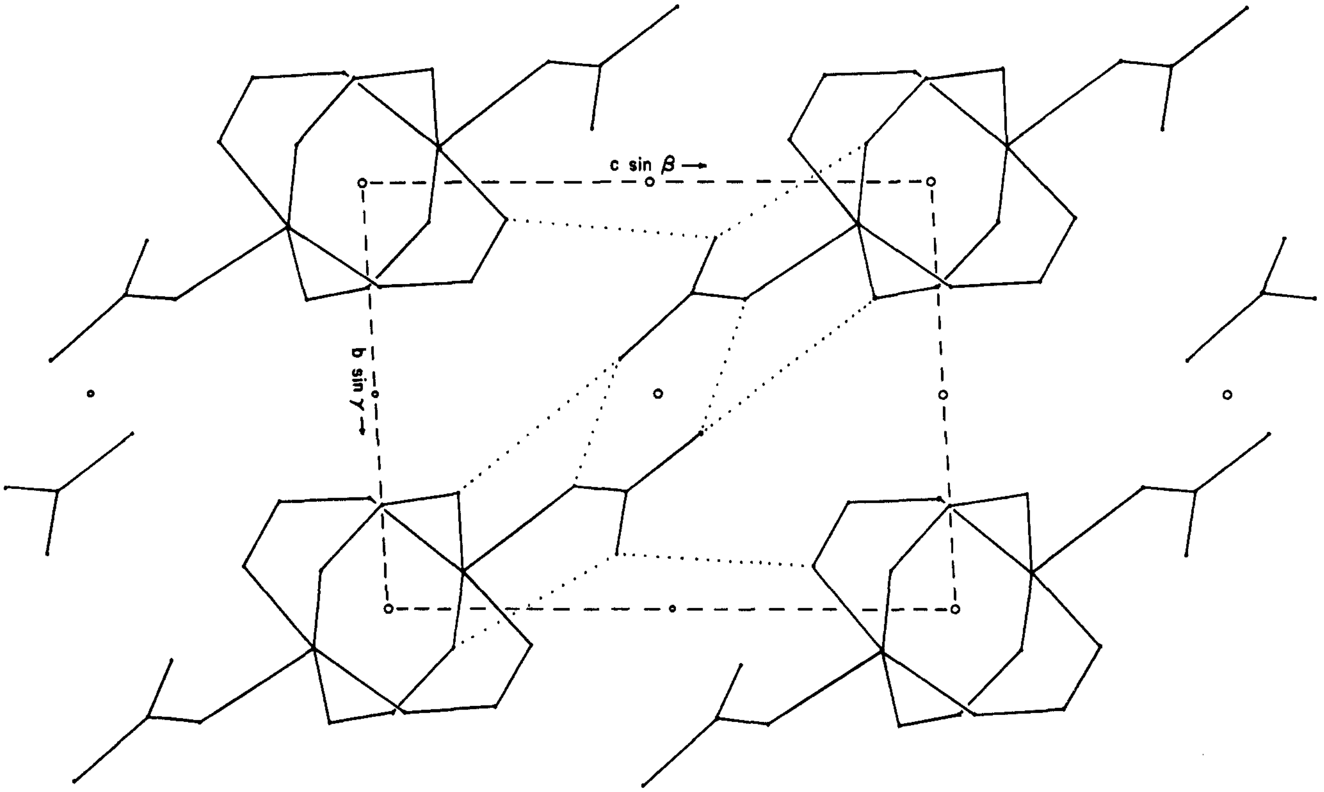

Figure 2.—Projection of the structure of copper(II) formate monourea onto a plane perpendicular to the [100] direction.

0.05 Å longer than is commonly found in bridged cupric carboxylates.

The configuration of the urea addend was another source of interest in the structure of copper(II) formate monourea. The structure of free urea has been ascertained with a high degree of accuracy[36] but very few reliable structural details are available on coordinated urea.[27-31]

The experimental treatment of the question of O bonding *vs.* N bonding of the urea ligand has already been discussed (*vide supra*). The important points to be reemphasized here are: (a) The precision of this structural analysis was not sufficient to permit the determination of hydrogen atom positions or an unequivocal distinction by other means between the oxygen and nitrogen atoms. (b) The atomic positional parameters (hence the derived bond lengths and angles) are invariant to which of the three possible urea models is chosen. (c) On the basis of isotropic thermal parameters for the urea oxygen and nitrogen atoms and other considerations to be outlined below, we consider the O-bonded model for the urea (model 3 of Table I) to be the most likely alternative and have labeled the atoms accordingly throughout this paper. Infrared spectral studies of cupric formate monourea have been carried out, but were inconclusive as to the mode of urea coordination.[26]

The urea ligand is directly bonded by O(5) to the copper atom [2.114 (13) Å] and is involved in a close intramolecular contact between N(1) and carboxylate oxygen O(4) [2.99 (2) Å]. While this latter interatomic distance exceeds the sum of two oxygen van der Waals radii (2.8 Å), it is in close agreement with reported distances for proposed nitrogen-to-oxygen hydrogen-bonding contacts in free urea.[36] The angles associated with the six-membered ring completed by this plausible intramolecular hydrogen bond are of some relevance. The Cu′–Cu–O(5) angle is not linear [174.0 (4)°], the O(5)–Cu–O(1–4) angles vary in the range 93.1 (6)–99.8 (6)°, and the Cu–O(5)–C(3) angle is 132.4 (13)° (these angles appear in Table IV). The least-squares plane containing the urea ligand is very nearly parallel to the plane containing the *trans*-carboxylate ring which incorporates O(4) (*cf.* planes 3 and 4, Table VI). The above structural features are consistent with the presence of the proposed intramolecular hydrogen bond between N(1) and O(4) and thus favor model 2 or model 3 (*cf.* Table I) for the urea coordination.

The bond distances within the urea ligand are C(3)–O(5) = 1.29 (2), C(3)–N(1) = 1.29 (2), and C(3)–N(2) = 1.34 (2) Å. These may be compared with the reported distances for free urea [C–O = 1.270 (7); C–N = 1.326 (6) Å[36]] and for O-coordinated urea in Ti(NH$_2$CONH$_2$)$_6$I$_3$ (C–O = 1.27; C–N = 1.33, 1.35 Å[31]).

The crystal packing of copper(II) formate monourea is depicted in the two projections of Figures 2 and 3. From these diagrams it can be seen that the crystal is built up of alternating layers of urea and Cu$_2$(O$_2$CH)$_4$ moieties (approximately perpendicular to the *c* axis). Intermolecular contacts up to 3.4 Å are

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(36) A. Caron and J. Donohue, *Acta Crystallogr.*, **17**, 544 (1964); *ibid.*, *Sect. B*, **25**, 404 (1969).

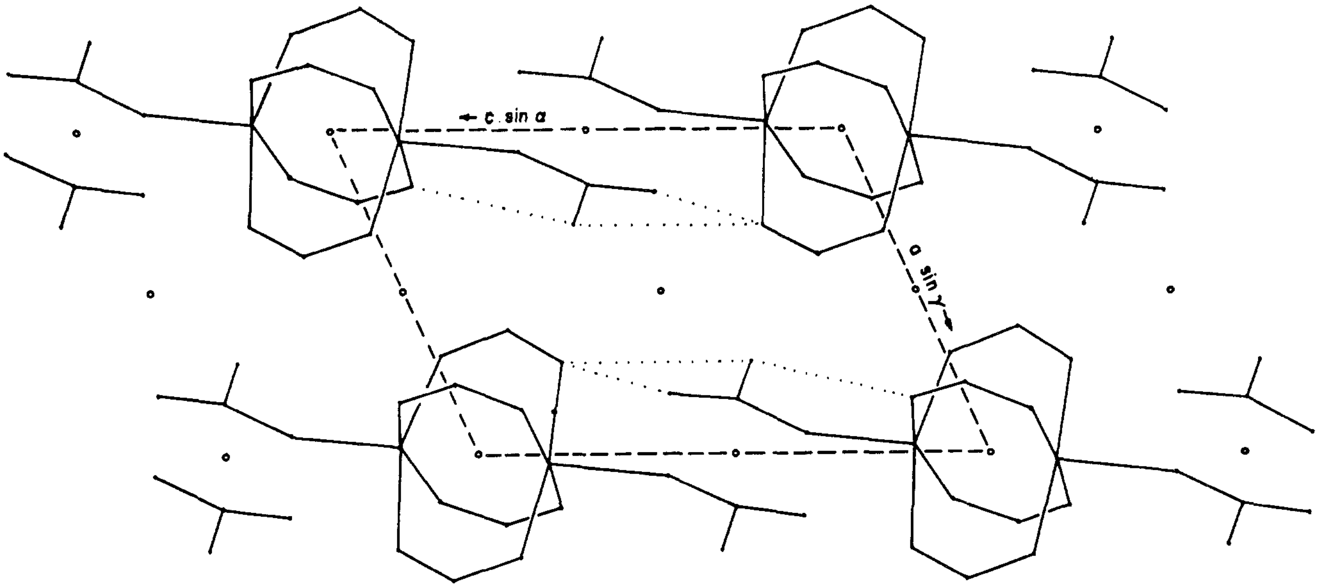

Figure 3.—Projection of the structure of copper(II) formate monourea onto a plane perpendicular to the [010] direction.

tabulated in Table V and the more plausible hydrogen-bonding interactions are illustrated in Figures 2 and 3.

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The Crystal and Molecular Structure of the Acetylacetonimine Adduct of Ytterbium Acetylacetonate, $Yb(C_5H_7O_2)_3(CH_3COCH{=}C(NH_2)CH_3)$

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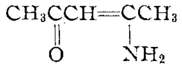
The crystal structure of tris(acetylacetonato)(4-amino-3-penten-2-one)ytterbium, $Yb(C_5H_7O_2)_3(CH_3COCH{=}C(NH_2)CH_3)$, has been determined from three-dimensional X-ray diffraction data. A total of 1301 independent nonzero reflections were collected by counter methods. Four formula units crystallize in a monoclinic unit cell with dimensions $a = 18.070$ (7), $b = 8.538$ (10), $c = 15.938$ (6) Å; $\beta = 99.13$ (10)°. The observed and calculated densities are both 1.56 g/cm^3; the space group is $P2_1/c$. The structure was refined by full-matrix least-squares methods to a conventional R factor of 0.073. The ytterbium atom is seven-coordinate, being bonded to six acetylacetonate oxygen atoms and the oxygen atom from the acetylacetonimine molecule. The coordination polyhedron is a capped trigonal prism, with an acetylacetonate oxygen as the capping atom. The NH_2 group in acetylacetonimine is hydrogen bonded to the acetylacetonate oxygen atoms in a glide-related molecule, thus linking the molecules in chains parallel to (100). The metal–acetylacetonate rings are folded about the O–O lines, at angles ranging from 10.1 to 19.6°. The Yb–O(acetylacetonimine) distance of 2.24 (2) Å is practically the same as the average of the six Yb–O(acetylacetonate) distances, 2.23 (2) Å.

In recent studies of rare earth acetylacetonates (Ln(acac)$_3$),[2] it was found that an acetylacetonimine (Hacim) solvate, with the formula Ln(acac)$_3$·Hacim, is fairly easily obtained for Yb and Lu by the ordinary Stites, McCarty, and Quill preparation method.[3] Both the Yb and Lu compounds can be recrystallized unchanged from acetylacetone and a variety of other solvents.[2] Infrared spectra[2] suggest that the Hacim exists in the amine tautomeric form, 4-amino-3-penten-2-one (**1**). The crystal structure of the Yb compound has been determined in order to discover what structure


$$\underset{\displaystyle \overset{\|}{O}}{CH_3C}CH{=}\underset{\displaystyle \overset{|}{NH_2}}{C}CH_3$$

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