Contribution from the Department of Chemistry,
Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

The Crystal and Molecular Structure of N,N′-Ethylenebis(acetylacetoneiminato)oxovanadium(IV)

By D. BRUINS and D. L. WEAVER

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The crystal and molecular structure of the compound VO($C_{12}H_{18}N_2O_2$), N,N′-ethylenebis(acetylacetoneiminato)oxovanadium(IV), VO(acen), has been determined by means of single-crystal X-ray diffractometry. The material crystallizes in the monoclinic space group $P2_1/a$ with a = 13.687 (3) Å, b = 11.957 (2) Å, c = 8.140 (1) Å, β = 93.76 (2)°, and Z = 4. The structure, including hydrogen atoms, was refined to an unweighted R factor of 7.5%. The coordination geometry around the vanadium atom is square pyramidal. An apical oxovanadium distance of 1.585 (7) Å was found. The basal plane of the pyramid, defined by two *cis* oxygen and two *cis* nitrogen atoms of the β-ketimine quadridentate ligand, lies 0.58 Å below the vanadium atom. When contrasted with the β-diketone derivatives of VO^{2+}, VO(acen) exhibits a surprising lack of solvent dependence of its spectral properties. A possible explanation can be found in the donor properties of the quadridentate ligand as reflected in the vanadium–basal ligand distances.

Introduction

Because of their stability and ready adaptability to study by a variety of spectroscopic techniques, oxovanadium(IV) complexes appear to be among the most thoroughly studied transition metal compounds.[1,2] One of the more interesting aspects of these complexes is the solvent dependence of their spectroscopic properties. For example, the square-pyramidal β-diketonates of VO^{2+} show pronounced solvent shifts of their visible, infrared, and esr spectral parameters.[1,3] These effects are attributed to axial ligation by the solvent molecule with attendant formation of a six-coordinate complex and change in the electronic structure.

It is therefore surprising to find that β-ketimine complexes such as N,N′-ethylenebis(acetylacetoneiminato)oxovanadium(IV), VO(acen), do not exhibit a similar dependence of spectral properties on solvent.[4] Geometric and/or electronic factors could be responsible for this behavior. In the case of trigonal-bipyramidal geometry,[5] such as that found for $VOCl_2(N(CH_3)_3)_2$, coordination by solvent in a sixth position appears to be sterically hindered. Neither would a solvent–complex interaction be expected for a dimeric species such as the tartrate,[6-8] $Na_4[VO\text{-}dl\text{-}tart]_2 \cdot 12H_2O$, or vanadyl complexes which are already six-coordinate.

A further reason for lack of solvent dependence could be due to charge build-up on the vanadium atom.[9-11] If the basal ligands are sufficiently strong donors and if vanadium–oxygen multiple bonding is to be maintained, axial coordination by a sixth ligand could be prevented. In order to determine which factors of the above (if any) are dominant for the complex VO(acen), a single-crystal X-ray study of this compound was undertaken.

Unit Cell Data and Collection of Intensities

A sample of VO($C_{12}H_{18}N_2O_2$), kindly supplied by Professor L. J. Boucher, was recrystallized from benzene. The systematic absences observed were $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, which are consistent with the space group $P2_1/a$. The equivalent positions of $P2_1/a$, an alternative setting of $P2_1/c$ (no. 14, $C_{2h}{}^5$), are: $\pm(x, y, z)$; $\pm(^1/_2 - x, ^1/_2 + y, \bar{z})$. The unit cell parameters were found to be a = 13.687 (3) Å, b = 11.957 (2) Å, c = 8.140 (1) Å, and β = 93.76 (2)° by least-squares refinement of 2θ values for 18 reflections, $59° \leq 2\theta \leq 80°$, centered on a GE XRD-5 diffractometer using Cu K$\bar{\alpha}$ radiation (λ 1.5418 Å) and a takeoff angle of 2°. A density of 1.44 (2) g/cm^3 was observed by flotation in a mixture of ethyl bromide and chlorobenzene, which agrees with the value of 1.45 g/cm^3 calculated for four molecules of VO(acen) in the unit cell.

A greenish black crystal of approximate dimensions 0.1 × 0.3 × 0.1 mm along a, b, and c, respectively, was mounted with its b axis coincident with the φ axis of a GE XRD-5 diffractometer for intensity measurement. The moving-crystal, moving-counter technique was used with a symmetric 2θ scan range of 3.0° and a scan rate of 2°/min. Upper and lower 10-sec stationary background counts were taken for each reflection at the extreme of the scan. The stability of the crystal was monitored by following intensities of three standard reflections at different positions in reciprocal space. These standard reflections were used to put all intensity data on a common scale. The maximum intensity variation during data collection was ±5%. No systematic trend was evident. Data were collected using Nb-filtered Mo Kα radiation with the pulse height analyzer set to accept about 90% of the Mo Kα radiation when centered on the peak. A takeoff angle of

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TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×10) FOR $VO(C_{12}H_{18}O_2N_2)$

H	L	FOBS	FCAL
**K =		0*****	
6	-8	278	-244
4	-8	176	-87
2	-8	203	189
0	-7	116	-124
2	-7	215	-229
4	-7	197	157
8	-7	383	394
10	-6	236	199
8	-6	355	-371
4	-6	424	-469
2	-6	122	-98
0	-6	256	262
2	-5	249	-253
4	-5	176	157
6	-5	430	422
10	-5	269	-292
12	-5	187	-214
12	-4	142	161
10	-4	170	119
6	-4	466	-495
4	-4	368	-326
2	-4	176	213
0	-3	406	-429
2	-3	514	-503
4	-3	987	946
6	-3	1048	1080
10	-3	282	-274
12	-3	223	-232
14	-3	211	-188
14	-2	225	275
12	-2	441	472
10	-2	205	183
8	-2	187	-191
6	-2	573	-564
4	-2	725	-689
2	-2	436	406
2	-1	613	-592
4	-1	951	890
6	-1	281	298
14	-1	141	-131
6	-1	301	298
0	-1	1493	-1534
2	0	1476	1362
4	0	1390	-1353
12	0	132	-105
10	0	216	-181
8	0	114	125
2	1	620	-624
4	1	277	263
6	1	781	812
8	1	401	386
12	1	177	-188
14	1	224	-239
14	2	280	285
12	2	399	426
8	2	297	-296
6	2	174	-198
4	2	245	-242
2	2	314	-294
0	2	285	263
8	3	358	365
10	3	122	93
12	3	398	-395
12	4	242	236
10	4	216	-204
8	4	561	-573
6	4	215	-208
0	4	460	461
0	5	314	-309
2	5	269	-266
6	5	342	346
8	5	334	348
10	5	132	-98
8	6	213	-229
6	6	181	-174
4	6	121	134
2	6	242	242
2	7	158	-186
8	7	233	186
2	8	248	253
0	8	305	288
**K =		1*****	
0	8	151	140
1	8	119	79
4	8	120	-78
6	7	236	205
4	7	213	138
4	6	383	-365
6	6	247	-293
8	6	170	150
10	6	359	352
9	5	126	-120
8	5	153	-113
6	5	295	273
4	5	539	524
2	5	248	256
1	5	140	123
1	4	368	-366
2	4	324	-339
3	4	139	-133
4	4	210	-217
6	4	252	-276
10	4	169	160
12	4	164	169
12	3	176	-182
10	3	329	-323
6	3	462	459
4	3	283	291
2	3	182	212
1	3	278	-283
1	2	807	811
2	2	1091	-1080
3	2	176	183
4	2	267	-262
5	2	221	-237
6	2	423	-422
7	2	200	-179
8	2	183	-179
9	2	113	69
10	2	346	357
12	2	244	257
13	2	176	-169
14	2	116	-92
12	1	299	-310
10	1	423	-446
8	1	243	-246
4	1	325	311
3	1	310	299
2	1	281	260
1	1	241	232
1	0	252	-246
2	0	886	-802
3	0	219	222
4	0	136	-119
6	0	503	471
8	0	353	358
10	0	416	397
12	0	215	214
14	0	165	-166
12	-1	285	-263
10	-1	302	-302
9	-1	109	-120
8	-1	346	-370
6	-1	343	-327
4	-1	385	358
3	-1	403	-396
2	-1	451	470
1	-1	132	145
0	-1	233	233
0	-2	643	628
2	-2	665	-656
4	-2	636	-599
5	-2	435	413
6	-2	191	-180
7	-2	200	200
8	-2	237	272
10	-2	383	402
12	-2	163	180
14	-2	165	-160
10	-3	178	-161
8	-3	436	-469
6	-3	163	153
5	-3	125	-116
4	-3	1243	1182
3	-3	134	124
2	-3	748	741
1	-3	201	-209
0	-3	252	-234
2	-4	755	-779
4	-4	532	-547
5	-4	196	-181
6	-4	157	141
7	-4	120	-93
8	-4	316	325
10	-4	116	163
11	-4	134	103
8	-5	229	-255
4	-5	494	498
2	-5	469	509
1	-5	159	176
0	-5	132	121
0	-6	264	-243
1	-6	139	-119
2	-6	220	-285
8	-6	171	158
10	-6	208	163
8	-7	304	-293
4	-7	152	128
2	-8	262	-242
5	-8	122	94
**K =		2*****	
8	-8	183	148
4	-8	208	269
2	-7	151	133
3	-7	249	-279
5	-7	123	-149
6	-7	244	-228
7	-7	160	90
8	-7	156	-128
9	-6	197	200
7	-6	134	-116
6	-6	276	275
1	-5	114	-114
2	-5	164	157
4	-5	307	-326
5	-5	234	227
6	-5	476	-467
7	-5	132	135
8	-5	119	-81
9	-5	113	-77
10	-5	196	207
12	-5	273	276
12	-4	305	-281
10	-4	199	-203
7	-4	134	-82
6	-4	408	408
4	-4	528	544
3	-4	402	407
1	-4	158	161
0	-3	312	313
2	-3	308	312
4	-3	283	-280
6	-3	627	-614
8	-3	206	-221
10	-3	284	295
12	-3	264	233
14	-2	245	-234
13	-2	126	90
12	-2	217	-243
9	-2	156	110
8	-2	332	344
6	-2	311	328
5	-2	261	-242
4	-2	99	137
3	-2	311	-318
2	-2	96	-62
1	-2	344	346
0	-1	732	717
1	-1	634	619
2	-1	228	-215
4	-1	408	-383
5	-1	96	86
6	-1	449	-463
7	-1	178	181
8	-1	222	-227
9	-1	155	-136
10	-1	151	-163
11	-1	204	-174
14	-1	239	206
12	0	266	-291
0	0	1211	-1317
11	0	120	-81
8	0	251	238
7	0	118	-121
6	0	550	544
4	0	491	478
3	0	452	449
2	0	871	-756
1	0	211	228
1	1	1074	-1034
2	1	1492	1426
3	1	837	-815
6	1	680	-683
8	1	337	-336
10	1	123	153
11	1	145	97
12	1	261	237
14	1	169	148
12	2	219	-225
9	2	136	-157
8	2	384	401
7	2	114	-94
6	2	368	382
3	2	394	408
2	2	624	-608
1	2	161	103
0	2	1136	-1145
2	3	298	284
4	3	138	113
6	3	489	-494
7	3	157	-133
12	3	231	225
12	4	151	-138
8	4	221	226
7	4	128	-33
6	4	250	247
5	4	164	-96
2	4	107	72
1	4	193	189
0	4	274	-315
0	5	244	241
2	5	239	248
5	5	131	114
6	5	267	-276
7	5	185	178
8	5	126	-140
8	6	317	318
6	6	172	174
2	6	383	-392
0	6	206	-177
0	7	170	185
2	7	249	255
4	7	160	147
2	8	213	-208
0	8	349	-321
**K =		3*****	
2	8	150	148
4	8	196	188
6	7	136	-142
4	7	204	-213
4	6	261	288
6	6	146	132
11	5	118	96
10	5	147	96
8	5	231	200
4	5	443	-447
2	5	220	-218
1	4	154	147
2	4	576	615
4	4	503	525
6	4	138	118
7	4	124	114
9	4	172	65
10	4	215	-165
12	4	146	-151
12	3	222	161
10	3	211	206
8	3	181	177
6	3	114	-80
5	3	196	163
4	3	719	-762
3	3	183	154
2	3	625	-668
1	2	401	399
3	2	505	502
4	2	657	632
5	2	203	186
6	2	152	153
8	2	372	-294
10	2	309	-303
12	2	115	-91
14	1	127	-105
11	1	183	-179
10	1	401	397
9	1	141	-178
8	1	568	574
7	1	100	-129
6	1	513	-495
5	1	488	-434
4	1	1005	-957
3	1	780	-762
2	1	379	351
1	1	287	-289
1	0	776	-755
2	0	1295	1259
4	0	522	524
6	0	111	84
8	0	384	-407
10	0	339	-347
12	0	151	-105
14	-1	136	-66
12	-1	152	119
10	-1	434	440
9	-1	258	229
8	-1	298	298
7	-1	326	328
6	-1	290	-305
5	-1	96	86
4	-1	361	-357
3	-1	87	-54
2	-1	155	-169
1	-1	466	451
0	-1	309	-311
0	-2	88	57
1	-2	301	-304
2	-2	158	170
3	-2	230	-240
4	-2	449	450
6	-2	269	269
7	-2	330	-338
8	-2	359	-344
9	-2	329	-338
10	-2	600	-599
14	-2	368	244
12	-3	128	-82
10	-3	222	280
8	-3	482	473
6	-3	157	149
4	-3	647	-650
3	-3	104	89
2	-3	533	-542
0	-4	178	210
2	-4	507	547
3	-4	166	-144
4	-4	257	270
8	-4	195	-201
10	-4	181	-154
10	-5	221	239
8	-5	251	273
4	-5	291	-290
2	-5	446	-466
0	-5	369	-353
0	-6	394	411
2	-6	475	494
5	-6	152	135
6	-6	130	-102
8	-6	170	-162
10	-6	238	-240
8	-7	204	166
2	-7	154	-144
0	-7	130	-129
2	-8	167	150
**K =		4*****	
4	-8	286	-287
0	-8	265	240
0	-7	143	-152
1	-7	133	117
3	-7	131	92
4	-7	167	156
6	-7	232	211
7	-6	115	-24
3	-6	152	-113
1	-5	277	282
4	-5	147	187
6	-5	162	179
8	-5	148	131
9	-5	152	-80
12	-4	260	269
8	-4	282	-259
6	-4	251	-233
4	-4	205	-203
3	-4	105	30
2	-4	170	-154
1	-4	250	-283
1	-3	383	-360
3	-3	267	-269
6	-3	496	515
8	-3	460	424
12	-3	254	-286
13	-3	148	99
13	-2	155	-128
12	-2	332	335
8	-2	623	-625
7	-2	119	-174
6	-2	336	-362
4	-2	122	153
1	-2	226	218
3	-2	198	178
1	-1	161	182
2	-1	159	-156
3	-1	441	-428
4	-1	109	-66
6	-1	336	360
5	-1	196	-177
7	-1	229	232
8	-1	262	269
10	-1	171	-173
12	-1	238	-250
12	0	267	255
10	0	195	195
9	0	214	211
8	0	220	-236
6	0	612	-612
5	0	160	-149
4	0	557	-545
2	0	147	156
0	0	532	536
0	1	229	-222
1	1	185	-175
2	1	816	-782
3	1	535	526
4	1	159	-143
5	1	612	598
6	1	652	688
7	1	294	-299
8	1	361	395
9	1	217	-228
12	1	139	-139
12	2	202	188
11	2	157	97
9	2	196	205
8	2	382	-378
6	2	498	-509
5	2	356	-362
3	2	138	-118
2	2	594	587
1	2	250	254
0	2	280	303
0	3	119	-121
1	3	103	91
2	3	594	-607
3	3	334	355
4	3	205	-233
5	3	203	198
6	3	418	409
8	3	281	304
12	3	207	-194
7	4	118	131
6	4	122	-134
3	4	342	-351
2	4	452	476
0	4	338	345
0	5	360	-371
1	5	159	-127
2	5	409	-420
3	5	128	-73
4	5	159	136
6	5	392	411
8	5	162	198
8	6	233	-246
6	6	303	-299
4	6	140	-94
2	6	300	294
1	6	115	93
0	6	329	337
0	7	169	-152
2	7	135	-102
2	8	131	134
0	8	231	240
**K =		5*****	
0	7	163	-146
1	6	165	-160
2	6	142	-146
4	6	270	-283
5	6	134	184
10	5	154	-107
8	5	225	-205
7	5	218	-195
5	5	334	-358
4	5	349	391
1	4	240	-219
2	4	354	-367
4	4	430	-416
5	4	170	152
10	4	139	121
12	3	129	-99
10	3	237	-241
8	3	274	-263
6	3	267	249
5	3	117	133
4	3	483	486
3	3	162	218
2	3	167	186
1	2	157	-127
2	2	370	-404
3	2	293	-306
4	2	163	-154
8	2	237	261
10	2	359	323
12	2	171	126
10	1	280	-296
8	1	243	-265
7	1	147	-164
6	1	224	238
5	1	121	-145
4	1	876	861
3	1	145	132
2	1	641	650
2	0	621	-621
3	0	190	-191
4	0	662	-687
6	0	186	-220
7	0	173	143
8	0	219	221
13	0	357	304
11	-1	148	132
10	-1	193	-152
8	-1	237	-190
7	-1	166	-172
6	-1	134	155
4	-1	441	439
3	-1	315	333
1	-1	98	124
1	-2	275	273
2	-2	116	-81
3	-2	308	-323
4	-2	270	-271
6	-2	184	-132
7	-2	322	294
8	-2	351	356
9	-2	147	147
10	-2	363	378
11	-3	168	101
10	-3	397	-422
9	-3	172	-177
8	-3	438	-491
7	-3	424	-414
5	-3	170	-134
4	-3	266	279
2	-3	286	285
1	-3	158	-169
0	-3	135	122
0	-4	178	-202
1	-4	110	-99
2	-4	557	-564
4	-4	195	-177
5	-4	129	144
7	-4	124	87
10	-4	228	213
11	-4	135	-88
8	-5	190	-168
7	-5	240	217
6	-5	244	-233
5	-5	136	123
4	-5	183	148
3	-5	140	-204
2	-5	413	438
1	-5	158	-147
0	-5	186	-207
0	-6	278	-301
2	-6	340	-329
5	-6	210	-189
6	-6	201	177
7	-6	151	-146
8	-6	164	189
4	-7	233	226
2	-7	251	295
1	-7	128	82
0	-7	139	146
2	-8	305	-264
**K =		6*****	
4	-7	174	-153
6	-7	176	-177
8	-6	183	144
4	-6	233	272
1	-5	185	-192
4	-5	211	-189
6	-5	350	-341
7	-5	149	-118
8	-5	127	-175
8	-4	123	76
4	-4	168	179
3	-4	129	136
2	-4	142	-130
1	-3	208	237
2	-3	187	226
3	-3	169	176
4	-3	254	-250
5	-3	135	-129
6	-3	314	-300
10	-3	128	93
12	-3	125	151
12	-2	271	-260
9	-2	127	-146
8	-2	417	405
6	-2	361	357
4	-2	202	182
3	-2	308	-315
1	-2	108	-109
4	-1	213	-212
6	-1	319	-328
7	-1	172	162
8	-1	303	-295
9	-1	141	97
12	-1	231	230
12	0	195	-217
8	0	189	200
7	0	112	-122
6	0	354	392
4	0	482	511
3	0	212	236
0	0	528	-546
0	1	254	252
2	1	550	587
3	1	241	-234
4	1	214	218
6	1	413	-472
8	1	206	-217
10	1	182	149
12	1	215	206
12	2	186	-190
9	2	194	-227
8	2	217	197
4	2	325	314
5	2	242	254
2	2	419	-431
0	2	349	-346
0	3	468	500
2	3	341	368
3	3	150	131
4	3	167	-161
6	3	359	-355
8	3	241	-245
10	3	120	-62
11	3	133	88
8	4	197	174
5	4	128	157
2	4	346	-366
0	4	517	-566
0	5	303	323
1	5	196	225
2	5	250	242
3	5	155	-136
5	5	174	-227
6	5	218	-163
8	5	201	-186
2	6	201	-168
1	6	130	-91
0	6	328	-316
6	6	125	82
**K =		7*****	
3	7	161	-154
2	6	136	123
4	6	252	209
6	6	206	217
8	5	150	119
7	5	117	98
2	5	139	-114
1	4	148	129
2	4	192	194
3	4	188	-193
5	4	245	-211
7	4	123	-64
10	3	166	193
9	3	138	84
7	3	111	-81
4	3	332	-344
2	3	304	-318
2	2	369	372
4	2	410	407
5	2	108	98
9	2	117	-98
10	2	198	-192
10	1	177	205
9	1	122	-98
8	1	135	135
7	1	109	94
6	1	265	-286
5	1	201	207
4	1	502	-518
2	1	220	-257
1	1	261	-256
1	0	369	379
2	0	392	404
4	0	255	272
8	0	214	-188
9	0	132	-35
10	0	243	-293
12	0	129	-110
10	-1	164	183
6	-1	114	-120
4	-1	267	-285
3	-1	120	136
2	-1	314	-332
1	-1	195	-194
1	-2	147	143
2	-2	505	509
4	-2	325	327
5	-2	179	-195
6	-2	118	140
10	-2	159	-194
12	-2	120	-99
10	-3	148	159
8	-3	278	269
7	-3	175	172
6	-3	175	161
5	-3	317	309
4	-3	290	-260
2	-3	279	-300
1	-3	162	-185
**K =		8*****	
6	-4	189	149
**K =		7*****	
2	-4	328	337
3	-4	152	-107
4	-4	135	144
5	-4	245	-238
6	-4	242	-226
8	-4	337	-313
9	-4	163	129
10	-4	176	-179
8	-5	312	319
6	-5	188	157
4	-5	162	-183
2	-6	260	241
4	-6	152	123
7	-6	120	-73
4	-7	247	-225
2	-7	131	-166
**K =		8*****	
6	-6	211	-192
5	-6	128	-143
4	-6	208	-179
2	-5	143	-136
3	-5	125	85
4	-5	196	188
6	-5	263	231
7	-5	124	-77
6	-4	142	-114
7	-4	254	252
6	-4	170	-124
3	-4	269	-257
2	-4	286	215
2	-3	140	-164
3	-3	213	226
4	-3	125	131
5	-3	188	189
6	-3	296	307
8	-3	192	148
10	-3	122	-123
6	-2	298	-268
4	-2	231	-241
3	-2	144	-154
1	-2	146	-168
0	-2	390	397
1	-1	276	291
2	-1	109	-108
3	-1	164	182
4	-1	134	153
5	-1	211	-187
6	-1	283	278
7	-1	115	-113
10	-1	135	-64
11	-1	129	-103
11	0	152	79
7	0	172	152
9	0	123	32
6	0	362	-343
5	0	241	276
4	0	248	-239
2	0	179	197
1	0	123	-149
0	0	382	384
0	1	276	-286
2	1	242	-226
4	1	273	223
6	1	356	310
7	1	146	-156
8	1	159	169
8	2	169	-146
7	2	141	-151
6	2	154	-137
5	2	237	-230
4	2	165	-177
3	2	243	-229
2	2	138	93
0	3	328	-349
1	3	137	98
2	3	285	-279
3	3	110	-60
4	3	121	-70
6	3	277	272
7	3	161	176
8	3	262	252
8	4	221	-166
7	4	118	-82
6	4	174	-151
2	4	288	280
1	4	169	-180
0	4	429	459
0	5	252	-251
2	5	164	-201
2	6	211	185
0	6	171	144
**K =		9*****	
2	6	180	-173
4	5	271	264
3	5	156	152
3	4	159	143
4	4	169	-183
6	4	147	-123
8	3	165	-149
4	3	114	142
3	3	197	-210
1	3	136	-134
2	2	131	-124
4	2	149	-128
6	2	134	-90
9	2	143	141
10	1	183	-117
8	1	144	161
4	1	276	286
3	1	139	-74
2	1	115	124
1	1	195	183
1	0	321	-331
2	0	405	-402
4	0	274	-281
10	0	169	87
10	-1	152	-151
8	-1	159	-176
5	-1	188	-177
4	-1	351	359
2	-1	268	253
1	-1	178	178
2	-2	237	-210
4	-2	292	-285
8	-2	207	201
10	-2	258	252
8	-3	236	-222
4	-3	215	192
2	-3	199	160
1	-3	165	196
0	-4	182	-153
1	-4	168	-207
2	-4	162	-143
4	-4	112	-56
5	-4	262	257
8	-4	129	115
4	-5	167	134
2	-6	128	-156
**K =		10*****	
6	-4	214	210
3	-4	147	134
2	-3	157	137
3	-3	191	-206
5	-3	205	-185
6	-3	273	-245
6	-2	138	117
2	-2	165	-185
0	-1	195	160
1	-1	153	-147
2	-1	205	218
6	-1	208	-192
8	-1	136	-84
8	0	161	153
6	0	184	233
3	0	209	214
1	0	161	183
0	0	323	-292
1	1	157	-113
3	1	199	-250
4	1	153	-125
6	1	289	-314
7	1	164	190
8	1	157	-211
9	1	136	93
8	2	148	154
6	2	231	234
4	2	120	103
2	2	149	-175
0	2	253	-257
0	3	188	201
2	3	278	278
6	3	174	-163
5	4	134	59
3	4	121	130
2	4	169	-169
0	4	196	-172
0	5	129	118
2	5	168	156
**K =		11*****	
3	4	122	-21
4	3	204	-183
2	2	165	154
4	2	148	128
7	1	117	114
5	1	124	86
4	1	155	-125
8	1	179	171
4	0	218	190
4	-1	250	-255
2	-1	220	-254
0	-2	138	115
2	-2	283	287
4	-2	177	154
4	-3	176	-151
3	-3	122	-125
2	-3	168	-149
2	-4	158	103
**K =		12*****	
1	-2	126	-157
0	-1	163	-116
2	1	112	-84
3	1	150	98
1	2	153	167
0	2	260	244

4° was used. Mosaic spread of the crystal was checked by the ω-scan technique and found to cause a maximum half-height peak width of approximately 0.37° for a typical strong reflection. Ten reflections had intensities which exceeded the linear reponse range of the counter. These intensities were remeasured by reducing the amperage on the X-ray tube until all reflections fell within the range of linearity.

All of the 1873 independent reflections for $2\theta_{\mathrm{MoK}\alpha} \leq 45°$ $[(\sin\theta)/\lambda \leq 0.54]$ were collected. These intensities were then corrected for background and reduced to values of F^2 by application of the Lorentz and polarization factors using a program written by P. Isaacs and G. S. Smith and subsequently revised by R. F. Stewart. Standard deviations were assigned to each reflection on the basis of counting statistics in the program according to the formula

$$\sigma(I) = [\mathrm{CT} + 0.25(t_C/t_B)^2(B_1 + B_2) + (PI)^2]^{1/2}$$

where CT is the total integrated count in time t_C, t_B is the time required for each background count B_1 and B_2, and P is a factor introduced to correct for random fluctuations encountered during data collection. A value of 0.045 was chosen for P. Reflections having an intensity $I \leq 2.0\sigma(I)$ were classified as unobserved and were not included in the refinement of the structure. No corrections for absorption were made on this crystal, as $\mu = 7.9\ \mathrm{cm}^{-1}$ for Mo Kα radiation. Consideration of the maximum and minimum path lengths for the crystal shows the transmission factors to range from about 0.92 to 0.89.

Solution and Refinement of the Structure

A three-dimensional Patterson function was calculated using the 954 independent observed reflections. The vanadium atom was easily located from this Patterson map. A Fourier map, phased on the vanadium atom, revealed the locations of the five atoms surrounding the vanadium atom. After least-squares refinement of the positional and thermal parameters for the six atoms, the value of the discrepancy index $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was 38%. A difference electron density map was then computed which showed the positions of the 12 carbon atoms. Three cycles of least-squares refinement of positional and isotropic thermal parameters for all of the 18 atoms led to values of R_1 of 11.1% and a weighted agreement factor, $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$, of 11.6%. At this point some punching errors were corrected and the vanadium and vanadyl oxygen atoms were refined with anisotropic thermal parameters, yielding an R_1 of 9.2%. Another difference Fourier map was computed, in which 18 of the 27 highest peaks, which ranged in density from 0.72 to 0.41 in e⁻/Å³, corresponded to reasonable positions for hydrogen atoms on the β-ketimine ligand.

The 18 hydrogen atoms were then included in the refinement. Their positional parameters were allowed to vary, but their thermal parameters were fixed at 1

TABLE II

FINAL POSITIONAL AND THERMAL PARAMETERS[a]

Atom	*x*	*y*	*z*	*B*,[b] Å^2
V	0.07702 (12)	0.25543 (18)	0.48685 (22)	2.62[c]
O_3	0.1388 (5)	0.1605 (6)	0.5815 (9)	3.23[c]
O_1	0.1234 (4)	0.2783 (5)	0.2685 (8)	2.94 (15)
O_2	0.1426 (5)	0.3965 (6)	0.5464 (9)	3.32 (17)
N_1	0.4611 (6)	0.3312 (7)	0.3744 (11)	3.07 (19)
N_2	0.4677 (6)	0.1973 (7)	0.6324 (10)	2.96 (18)
C_1	0.1590 (9)	0.2562 (14)	0.9920 (15)	4.15 (24)
C_2	0.0968 (7)	0.2291 (9)	0.1296 (12)	2.98 (21)
C_3	0.0136 (9)	0.1653 (10)	0.1066 (15)	4.15 (28)
C_4	0.4478 (8)	0.3631 (9)	0.2229 (14)	3.30 (24)
C_5	0.3634 (12)	0.4353 (13)	0.1716 (21)	5.44 (36)
C_6	0.3932 (12)	0.3648 (14)	0.5039 (21)	6.23 (41)
C_7	0.3835 (9)	0.2794 (11)	0.6231 (16)	4.41 (30)
C_8	0.4616 (8)	0.1066 (9)	0.7187 (13)	3.00 (23)
C_9	0.3724 (10)	0.0823 (13)	0.8176 (17)	4.38 (31)
C_{10}	0.0367 (9)	0.4718 (10)	0.7310 (15)	3.46 (28)
C_{11}	0.1218 (8)	0.4710 (9)	0.6540 (13)	2.85 (22)
C_{12}	0.2984 (12)	0.0540 (14)	0.3054 (19)	4.92 (35)
H_{11}[d]	0.1314 (73)	0.2124 (83)	0.904 (12)	
H_{12}	0.2297 (72)	0.2294 (84)	0.018 (11)	
H_{13}	0.1763 (75)	0.3379 (90)	0.991 (13)	
H_{31}	0.0102 (78)	0.1348 (89)	0.002 (14)	
H_{51}	0.3045 (86)	0.4024 (99)	0.212 (14)	
H_{52}	0.3629 (79)	0.4196 (94)	0.035 (14)	
H_{53}	0.1134 (90)	0.005 (10)	0.832 (15)	
H_{61}	0.4333 (84)	0.4329 (99)	0.545 (14)	
H_{62}	0.3542 (80)	0.3336 (93)	0.427 (13)	
H_{71}	0.4141 (90)	0.322 (11)	0.697 (15)	
H_{72}	0.3451 (68)	0.2701 (90)	0.740 (13)	
H_{91}	0.3883 (77)	0.1354 (90)	0.908 (13)	
H_{92}	0.3259 (77)	0.0853 (91)	0.739 (13)	
H_{93}	0.3847 (78)	0.018 (10)	0.860 (13)	
$H_{10,1}$	0.4769 (76)	0.0190 (88)	0.211 (12)	
$H_{12,1}$	0.3317 (82)	0.1095 (99)	0.286 (14)	
$H_{12,2}$	0.2820 (83)	0.0644 (99)	0.398 (14)	
$H_{12,3}$	0.2604 (80)	0.0219 (88)	0.201 (14)	

Anisotropic Temperature Parameters[e] (× 10^4)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
V	27.3 (9)	53.7 (14)	105.7 (27)	3.0 (15)	8.1 (11)	−6.4 (26)
O_3	37.9 (48)	67.5 (71)	112.3 (15)	4.7 (5)	−2.4 (7)	−17.0 (8)

[a] Numbers in parentheses are esd's in the last figure quoted. [b] Hydrogen atom temperature factors were not refined but were given a *B* value one unit greater than the carbon atom to which they were attached. [c] Equivalent isotropic *B*'s are quoted here for the anisotropically refined atoms. [d] The first subscript in the designation of each hydrogen atom refers to the carbon atom to which it is bonded. [e] Anisotropic temperature factors are of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

unit greater in *B* than the value for the carbon atom to which they were attached. Seven more cycles of full-matrix least-squares refinement, in which the positional parameters for all atoms including hydrogen, as well as the thermal parameters for all atoms but hydrogen, were varied, led to final $R_1 = 7.5\%$ and $R_2 = 6.8\%$. The maximum shift in bond distances upon inclusion of the hydrogen atoms in the refinement was 1.8 σ, the average change being 0.7 σ. During the final cycle of refinement no positional or thermal parameter shifted by more than 33% of its estimated standard deviation, the average change being approximately 2%. A final difference Fourier map was essentially featureless with the highest peak, which was in the vicinity of the vanadium atom, having a value of 0.52 e$^-$/Å^3. A calculation of the structure factors for the 919 unobserved data gave two reflections with an $|F_c|$ greater than twice the minimum observable.

TABLE III

PRINCIPAL MOLECULAR DIMENSIONS[a]

Bond distances, Å				Intramolecular nonbonded contacts, Å	
V–O_1	1.945 (7)	N_2–C_7	1.512 (15)	O_1–N_1	2.764 (11)
V–O_2	1.956 (8)	C_2–C_3	1.373 (16)	O_2–N_2	2.774 (11)
V–O_3	1.585 (7)	C_{10}–C_{11}	1.359 (16)	O_1–O_2	2.665 (10)
V–N_1	2.059 (9)	C_3–C_4	1.391 (17)	N_1–N_2	2.638 (12)
V–N_2	2.048 (8)	C_8–C_{10}	1.389 (16)	O_3–O_1	2.907 (9)
O_1–C_2	1.305 (12)	C_6–C_7	1.421 (21)	O_3–O_2	2.837 (11)
O_2–C_{11}	1.294 (13)	C_1–C_2	1.487 (16)	O_3–N_1	2.869 (11)
N_1–C_4	1.292 (14)	C_4–C_5	1.480 (19)	O_3–N_2	2.946 (11)
N_2–C_8	1.298 (14)	C_8–C_9	1.534 (17)	O_1–N_2	3.772 (10)
N_1–C_6	1.505 (19)	C_{11}–C_{12}	1.497 (20)	O_2–N_1	3.884 (11)

Interbond angles, deg			
O_3–V–O_1	110.4 (3)	C_3–C_4–N_1	121.3 (1.0)
O_3–V–O_2	106.0 (3)	C_5–C_4–N_1	120.0 (1.0)
O_3–V–N_1	103.1 (4)	C_9–C_8–C_{10}	116.4 (1.0)
O_3–V–N_2	107.7 (4)	C_{10}–C_8–N_2	122.0 (1.0)
O_2–V–N_1	150.7 (3)	C_9–C_8–N_2	121.6 (1.0)
O_1–V–N_2	141.6 (3)	V–O_1–C_2	129.7 (0.6)
O_1–V–N_1	87.3 (3)	V–O_2–C_{11}	130.0 (0.7)
N_1–V–N_2	79.9 (3)	V–N_1–C_4	129.0 (0.8)
N_2–V–O_2	87.7 (3)	V–N_2–C_8	128.2 (0.7)
O_2–V–O_1	86.2 (3)	V–N_1–C_6	108.4 (0.8)
O_1–C_2–C_1	114.4 (1.1)	V–N_2–C_7	112.0 (0.7)
O_1–C_2–C_3	123.4 (1.0)	C_6–N_1–C_4	122.3 (1.0)
C_1–C_2–C_3	122.0 (1.1)	C_7–N_2–C_8	119.6 (0.9)
O_2–C_{11}–C_{12}	114.6 (0.6)	C_2–C_3–C_4	127.7 (1.2)
O_2–C_{11}–C_{10}	123.4 (1.0)	C_8–C_{10}–C_{11}	127.9 (1.1)
C_{12}–C_{11}–C_{10}	121.9 (0.6)	N_1–C_6–C_7	112.1 (0.7)
C_3–C_4–C_5	118.6 (1.1)	C_6–C_7–N_2	113.3 (1.1)

[a] Standard deviations of least significant figures are given in parentheses.

Throughout the solution and refinement of the structure, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with the weight equal to $4F_o^2/\sigma^2(F_o^2)$. The final error in an observation of unit weight is 1.55. Scattering factors used for the O, N, and C atoms were those tabulated by Ibers;[12] the factor for the vanadium atom was taken from calculations of Cromer and Waber.[13] The hydrogen atom scattering factors were those of Stewart, *et al.*[14] The corrections for anomalous dispersion of the vanadium atom are small ($\Delta f' = 0.31$ and $\Delta f'' = 0.60$ for Mo Kα) and none was applied. Computations were mainly performed on an IBM-360 computer. The major programs used were: Patterson and Fourier syntheses, Zalkin's FORDAP; structure factor and least-squares refinement, Prewitt's SFLS-5.

Table I lists the observed structure amplitudes, $10|F_o|$, and the final calculated structure factors, $10F_c$, each in electrons. The final fractional coordinates and thermal parameters for all atoms are given in Table II. The anisotropy of the thermal motion for the vanadium and oxygen (O_3) atoms is small. The major axis of the atomic thermal ellipsoids for both atoms is very nearly parallel to *b*.

Results and Discussion

The crystal consists of discrete molecules of VO(acen) which have no crystallographic symmetry; the very approximate C_s symmetry of the molecule is largely destroyed by twisting of the ethylene group about the carbon–carbon bond. Selected interatomic bond distances and angles along with their standard deviations are given in Table III. A view of the molecule pro-

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(12) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202.

(13) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

(14) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

jected down the crystallographic *b* axis is shown in Figure 1, which also includes the atom designations.

The coordination figure around the central vanadium atom is basically a square pyramid formed by the two oxygen and two nitrogen atoms of the quadridentate ligand at average distances of 1.950 (6) and 2.053 (6) Å, respectively. An apical vanadyl oxygen atom completes the square pyramid at a distance of 1.585 (7) Å from the vanadium atom, which is within the range 1.56–1.67 Å reported for other vanadyl complexes. The vanadium atom is displaced 0.58 Å above the least-squares plane of the four coordinating atoms (O_1, O_2, N_1, and N_2) of the β-ketimine. The coordination pyramid surrounding the vanadium atom is shown in Figure 2 along with those for bis(acetylacetonato)oxovanadium(IV), $VO(acac)_2$,[15] and *cis*-bis(1-phenyl-1,3-butanedionato)oxovanadium(IV), $VO(bzac)_2$.[16] The pyramid in VO(acen) very closely approximates those found in the β-diketone complexes. The distances between the coordinated N and O atoms (the "bite distance" of the chelating rings) are quite similar to the O–O distances in the β-diketonates, which also contain six-membered chelate rings. However, the O–O distances in the tartrate[7] complex $Na_4[VO\text{-}dl\text{-}tart]_2 \cdot 12H_2O$, which contains a five-membered ring, are smaller than in either of the other three complexes. It may be noted that $VO(acac)_2$ has been described as a distorted trigonal bipyramid by at least one group of authors.[17] However, if we choose what appears to be a reasonable[18,19] apex-to-base angle (vanadyl oxygen–V–basal ligand angle) of ≥ 90 and $\leq 115°$ for a square-pyramidal configuration, the angular distortions from a trigonal bipyramid are much greater than those for the square pyramid in both $VO(acac)_2$ and VO(acen).

Bond distances within the β-ketimine do not differ significantly from those previously determined for three[20–22] copper derivatives of this ligand. The average C–N and C–O bond distances of 1.29 (1) and 1.30 (1) Å, respectively, agree with those found for a series of salicylaldimine complexes. A survey[23] by Lingafelter and Braun of eight three-dimensional determinations of salicylaldimates gives an average of 1.295 Å for the C–N bond and 1.312 Å for the C–O bond, which correspond to bond orders of approximately 1.8 and 1.5, respectively.

The ethylenediamine portion of the quadridentate ligand assumes a configuration approximately halfway between *gauche* and eclipsed, as the torsion angle between the carbon–nitrogen bonds is 33.3°. The two carbon atoms C_6 and C_7 are 0.77 and 0.53 Å, respectively, above the plane containing the vanadium and two nitrogen atoms. The dihedral angle[24] between the N_1–V–N_2 and the C_6–V–C_7 plane is 17.8°. No isolated portion of the molecule is exactly planar, as indicated by the equations for the weighted least-squares planes given in Table IV. The acetylacetoneiminatovanadium rings exhibit a folding along the oxygen–nitrogen line which is comparable to that found in many β-diketone complexes.[25] The dihedral angle between the plane containing the O_1–N_1 portion of the ligand and the plane defined by the O_1–V–N_1 group is 16.0°, whereas the comparable angle which measures folding along the O_2–N_2 line is 19.3°. The angle between the planes O_1–V–N_1 and O_2–V–N_2 is 132.3° which can be compared with 134.7°in VO $(acac)_2$ and 135.6° in $VO(bzac)_2$.

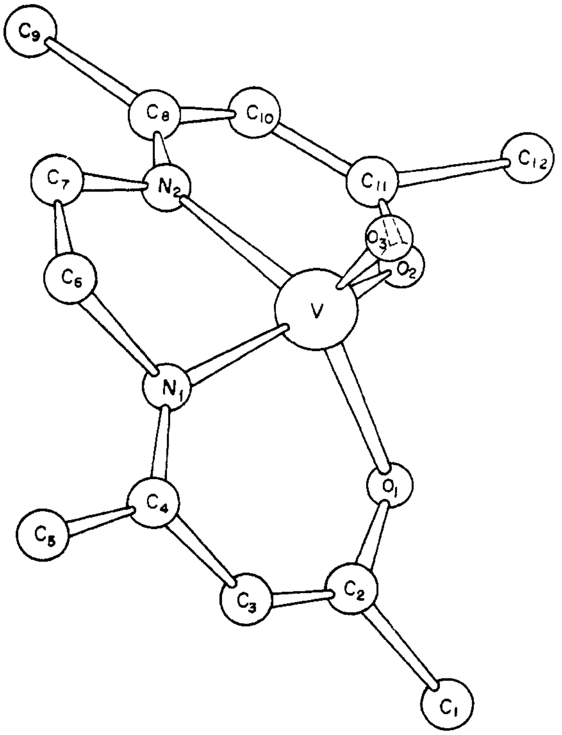

Figure 1.—A view of a molecule of VO(acen) projected on the crystallographic *ac* plane.

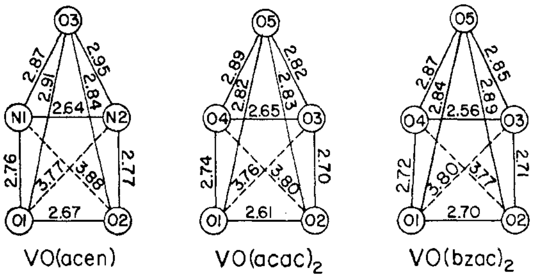

Figure 2.—A comparison of the coordination pyramid in VO(acen), $VO(acac)_2$, and $VO(bzac)_2$ (acac = acetylacetonate; bzac = benzoylacetonate). Average standard deviations are 0.01 Å.

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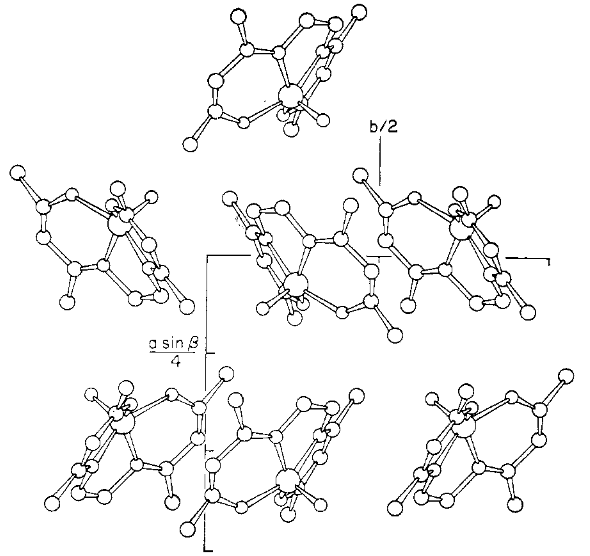


Figure 3.—Molecular packing for VO(acen) viewed down the crystallographic *c* axis.

Table IV

Weighted^{a} Least-Squares Planes of the Form $LX + MY + NZ = D^{b}$

Plane no.	Atoms	*L*	*M*	*N*	*D*
1	N_1, N_2, O_1, O_2	0.5242	−0.7107	0.4691	−0.4776
2	O_1, C_2, C_3, C_4, N_1	0.5420	−0.8047	0.2423	−1.300
3	O_2, C_{11}, C_{10}, C_8, N_2	0.4272	−0.5000	0.7533	1.702
4	C_2, C_1, C_3, O_1	0.5400	−0.8033	0.2513	−1.287
5	C_4, C_3, C_5, N_1	0.5269	−0.8201	0.2234	−1.363
6	C_8, C_9, C_{10}, N_2	0.3777	−0.4793	0.7922	2.038
7	C_{11}, C_{10}, C_{12}, O_2	0.3516	−0.5947	0.7230	0.9713
8	N_1, C_6, C_7	0.7382	−0.3844	0.5544	0.3706
9	C_6, C_7, N_2	0.4433	−0.5708	0.6912	1.139
10	C_6, V, C_7	0.3790	−0.5977	0.7065	1.270
11	N_1, V, N_2	0.1707	−0.7810	0.6007	0.1259
12	N_1, V, O_1	0.5219	−0.8482	0.0902	−1.819
13	N_2, V, O_2	0.4297	−0.4458	0.7852	2.085

Plane no.	Distances of atoms from planes, Å				
1	N_1, 0.086;	N_2, −0.094;	O_1, −0.054;	O_2, 0.061;	V, 0.58
2	O_1, −0.010;	C_2, 0.032;	C_3, −0.009;	C_4, −0.030;	N_1, 0.017
3	O_2, −0.020;	C_{11}, 0.047;	C_{10}, −0.003;	C_8, −0.046;	N_2, 0.024
4	C_2, 0.029;	C_1, −0.013;	C_3, −0.013;	O_1, −0.003	
5	C_4, −0.014;	C_3, 0.004;	C_5, 0.007;	N_1, 0.002	
6	C_8, −0.012;	C_9, 0.005;	C_{10}, 0.004;	N_2, 0.002	
7	C_{11}, −0.016;	C_{10}, 0.006;	C_{12}, 0.008;	O_1, 0.002	
11	C_6, 0.775;	C_7, 0.526			

Planes	Dihedral angle, deg	Planes	Dihedral angle, deg
8–9	33.3	3–13	19.3
10–11	17.1	12–13	132.3
2–12	16.0		

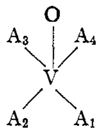
[a] Atoms are weighted by the reciprocals of their variances. [b] The matrix to transform from monoclinic to orthogonal coordinates is

$$\begin{matrix} 13.687 & 0 & -0.5332 \\ 0 & 11.957 & 0 \\ 0 & 0 & 8.122 \end{matrix}$$

A view of the crystal structure down the crystallographic *c* axis is given in Figure 3. In the solid there is not even weak coordination to the vanadium atom in the vacant position below the basal plane, the closest intermolecular distance of approach being that of a carbon atom (C_{10}) at 4.0 Å. There are two rather close intermolecular contacts between methyl groups in the crystal: C_5–C_9 = 3.68 Å and C_5–C_1 = 3.74 Å.

Table V

Comparison of Vanadium Coordination in VO(acen) with That Observed in VO(acac)$_2$ and VO(bzac)$_2$



Angles	Value, deg VO(acen)^{a}	VO(acac)$_2$^{b}	VO(bzac)$_2$^{c}
O–V–A_1	110.4 (3)^{d}	106.2 (4)	106.6 (4)
O–V–A_2	106.0 (3)	105.6 (4)	104.0 (4)
O–V–A_3	[103.1 (4)]^{e}	108.4 (4)	106.9 (4)
O–V–A_4	[107.7 (4)]	104.8 (4)	106.0 (4)
Av	106.8	106.2	106.0
A_1–V–A_2	86.2 (3)	83.5 (3)	85.8 (3)
A_2–V–A_3	[87.3 (3)]	87.8 (3)	87.5 (3)
A_3–V–A_4	[79.9 (3)]	83.9 (3)	82.2 (3)
A_4–V–A_1	[87.7 (3)]	86.9 (3)	87.3 (3)
Av	85.3	85.5	85.7
A_1–V–A_3	[150.7 (3)]	145.5 (3)	146.5 (3)
A_2–V–A_4	[141.6 (3)]	149.6 (3)	149.9 (3)
Av	146.1	147.5	148.2

Distances	Value, Å VO(acen)	VO(acac)$_2$	VO(bzac)$_2$
V–O	1.585 (7)	1.571 (10)	1.612 (10)
V–A_1	1.956 (8)	1.974 (8)	1.982 (8)
V–A_2	1.945 (7)	1.955 (8)	1.986 (7)
V–A_3	[2.059 (9)]	1.983 (7)	1.952 (8)
V–A_4	[2.048 (8)]	1.962 (7)	1.946 (8)
Distance of vanadium atom from basal plane	0.58	0.55	0.54

[a] For VO(acen) A_1, A_2, A_3, and A_4 correspond to O_2, O_1, N_1, and N_2, respectively. [b] Vanadyl(IV) bisacetylacetonate.[15] Values are those obtained from the anisotropic refinement of data of Dodge, *et al.;* *cf.* P. K. Hon, R. L. Belford, and C. E. Pfluger, *J. Chem. Phys.*, **43**, 3111 (1965). [c] Vanadyl(IV) bisbenzoylacetonate.[16] [d] Standard deviations of least significant figures are given in parentheses. [e] Values involving nitrogen atoms are enclosed in brackets.

Table V compares the bond distances and angles for VO(acen) with those of the two previously determined β-diketone structures. From Table V and Figure 2, one can see that there are no significant differences in the geometry between the three compounds. The averages for the various types of angles in these three square pyramids are equal within experimental error. In addition, molecular models indicate that there is no significant additional steric hindrance imposed by the ethylenediamine bridge (or by any other portion of the VO(acen) molecule) when one attaches a sixth ligand *trans* to the oxovanadium group. Consequently, there are no readily apparent steric reasons for the lack of solvent dependence of the spectroscopy for VO(acen) when compared with the large solvent shifts found for the β-diketone complexes.

Closer inspection of the bond distances in Table V reveals a possible explanation for this lack of solvent dependence, involving charge buildup (*vide supra*) on the central vanadium atom from the strong in-plane σ donation of the β-ketimine. If the multiple oxovanadium bond which dominates the ligand field is to be maintained, no axial coordination can occur. The average V–O and V–N in-plane distances of 1.950 (6) and 2.053 (6) Å, respectively, for VO(acen) are among the shortest determined for simple monomeric oxovanadium compounds.[26] They can be compared with the average of 1.969 (4) Å found for $VO(acac)_2$ and the average of 1.984 (6) Å determined in *cis*-$VO(bzac)_2$ for the two V–O distances on the side of the chelate rings to which the methyl groups are attached.[27] Similarly, the average V–N distance of 2.053 (6) Å is shorter than the average of 2.11 (1) Å found for three of the V–N bonds in an oxovanadium porphyrin complex.[28] Although the differences in bond lengths considered here are marginally significant (approximately 4–7 σ), they all indicate stronger coordination of the in-plane donor atoms in VO(acen). The vanadyl–apical oxygen bond order in all of these complexes appears to be sufficiently high so that this bond distance is relatively insensitive to other bonding variations.

Further support for the idea of electronic cause for the lack of coordination of a solvent with VO(acen) comes from the following evidence. (1) In solution, the interaction of $VO(acac)_2$ with base is greater than that for VO(acen). The experimental[29] heat of reaction (ΔH_{rxn}) for the addition of 2,4-dimethylpyridine N-oxide to $VO(acac)_2$ and VO(acen) in dichloromethane is -5.4 ± 0.1 and -0.07 ± 0.02 kcal/mol, respectively. (2) The complex[30] N,N′-ethylenebis(trifluoroacetylacetoneiminato)oxovanadium(IV), VO(tfen), shows solvent dependence of its spectroscopic properties. The strong electron-withdrawing power of the CF_3 groups seems to remove sufficient electron density from the vicinity of the vanadium atom so that a coordinating solvent can attach itself to the axial position. (3) The infrared and esr spectral parameters[30] for VO(acen) and VO(tfen) both indicate a stronger in-plane ligand field for the VO(tfen) complex. The V=O stretching frequency for VO(acen) is 982 cm^{-1}, whereas that for VO(tfen) is ~999 cm^{-1} in acetonitrile. Also, the isotropic hyperfine splitting parameter, A_0, is higher (104.6 G) in VO(tfen) than the 102.2 G found for VO(acen) under similar conditions. This is in accord with a smaller 4s contribution to the σ bonding in the VO(tfen) complex. (4) If axial ligation occurs in oxovanadium complexes, the vanadium atom moves closer to the plane of the basal ligands and thus acquires increased electron density. A recent structure determination[31] of $VO[(H_2O)_4SO_4]\cdot H_2O$, which has a water molecule bonded in the (normally vacant) axial position of the square pyramid, shows the vanadium atom to be 0.29 Å out of the basal plane as compared to the 0.59 Å found for VO(acen). The increase in charge density caused by movement of the vanadium atom toward the basal ligands seems to be a factor in preventing a coordination solvent from bonding to the sixth vacant axial position in VO(acen).

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(26) Shorter vanadium–ligand distances include the vanadium–hydroxyl oxygen distances in the dimericv anadyl complexes $(NH_4)_4[VO\text{-}d\text{-tart}]_2\cdot 2H_2O^6$ of 1.93 (2) and 1.79 (2) Å and $Na_4[VO\text{-}dl\text{-tart}]_2\cdot 12H_2O^7$ of 1.917 (6) and 1.902 (6) Å. A recent structural determination of the distorted square-pyramidal $Na((C_2H_5)_4N)[VO(benzilate)_2]\cdot 2C_3H_7OH$ [N. D. Chasteen, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, **8**, 408 (1969)] shows distances of 1.900 (8) and 1.933 (8) Å between vanadium and hydroxyl oxygen.

(27) In the latter compound the two vanadium–oxygen distances on the opposite side of the chelate ring were found to average 1.949 (6) Å. The authors concluded that this "anomalously short" V–O distance is due to a conjugative effect involving the phenyl group and the chelate ring which causes electron density drift into the V–O bonds.

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