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The Crystal Structure of Technetium(IV) Chloride. A New AB_4 Structure

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Crystal structure analysis of technetium(IV) chloride has established that it represents a new structure type for AB_4 compounds. Distorted octahedral units of composition $TcCl_6$ are linked to form polymeric chains, each octahedral unit sharing one edge with each of the two adjacent octahedra, while the two unshared chlorine atoms themselves form an edge. The repeating unit of the chain is a Tc_2Cl_8 unit made up of two $TcCl_4$ planar asymmetric units related to each other by a glide plane. There are three pairs of chemically distinct Tc–Cl bonds whose mean lengths are 2.24, 2.38, and 2.49 A, respectively. A possible explanation for these differences is offered in terms of varying degrees of π bonding.

Introduction

Prior to this investigation, preliminary results of which have been reported,[1] there was no direct structural knowledge concerning the tetrahalides of the manganese group elements Mn, Tc, and Re. Indeed, the existence of $MnCl_4$ is uncertain, and $ReCl_4$ has been obtained only as an amorphous powder. $TcCl_4$, which forms good single crystals, was therefore an attractive subject for structure analysis. Colton and Martin[2] have predicted a trinuclear structure for $ReCl_4$, similar to that of $(Re_3Cl_{12})^{3-}$,[3,4] to account for its low observed magnetic moment of 1.0 BM. An indication that the structure of $TcCl_4$ is unrelated to that of $ReCl_4$ is given by the magnetic moment of 3.48 BM ($\theta = -57°$) as reported by Knox and Coffey.[5] This value is in reasonable agreement with the value of 3.6 BM calculated by Figgis and Lewis[6] for Tc(IV) in an undistorted octahedral environment.

Experimental Section

The compound was prepared by Mrs. J. H. Hickford, following the method of Colton,[7] by passing chlorine over heated technetium metal and decomposing any remaining blue-green $TcCl_6$ by gentle heating. The resulting $TcCl_4$ was sublimed in the chlorine stream and dark red needle-shaped crystals were obtained. The compound is unstable in the presence of water vapor and the crystal used for X-ray data collection was sealed inside a thin-walled glass tube under an atmosphere of dry carbon dioxide. This crystal had an average cross-sectional diameter of 0.1 mm and was 1.5 mm long (parallel to the *c* axis).

Crystal Data.—$TcCl_4$, mol wt 240.8, is orthorhombic, having space group Pbca from systematic absences of X-ray reflections, $a = 11.65$, $b = 14.06$, $c = 6.03$ A, all with $\sigma = 0.01$ A (λ 0.7107 A for Mo Kα radiation), $U = 982.5$ A^3. D_m was established as being within the range 2.90 to 3.34 g cm^{-3} as the crystals sank in pure bromoform but floated in pure methylene iodide. $Z = 8$, $D_x = 3.26$ g cm^{-3}. The linear absorption coefficient is 53 cm^{-1} for Mo Kα radiation.

Intensity sets were collected on the Buerger precession camera for the reciprocal lattice levels $(0\ldots4kl)$ and $(h0\ldots5l)$, using Mo Kα radiation. Of a total of 790 independent reflections, 244 were recorded as unobserved and assigned an intensity one-third of the minimum observable. Intensities of the remainder were measured by visual comparison with a suitably calibrated scale. Absorption corrections were applied on the basis of a cylindrical crystal of radius 0.05 mm ($\mu R = 0.3$).

Structure Determination

The asymmetric unit in this structure consists of a single technetium atom and four chlorine atoms. All atoms were finally located on sets of eightfold general positions. Projections of the Patterson function down each of the three crystallographic axes were used to locate first the technetium atom and then the chlorine atoms. The correctness of a trial three-dimensional solution was confirmed by good structure factor agreement with part of the general diffraction data. The full precession data were then used for seven cycles of least-squares refinement using the block diagonal approximation with each atom assigned an individual isotropic temperature factor. A weighting scheme suggested by Mills and Rollett[8] was used, with $\sqrt{w} = 1$ for $F_o \leqslant 60$ and $\sqrt{w} = 60/F_o$ for $F_o > 60$. Interlevel correlation was achieved by scaling ΣF_o to $\Sigma|F_c|$ for each level at the start of the refinement. An acceleration procedure[9] was used and the R index dropped to 0.12. After rescaling to $\Sigma F_o = \Sigma|F_c|$ for each level, the unobserved data were removed. The same weighting scheme was kept and the 546 remaining reflections were used in four further least-squares cycles during which the R index fell from 0.105 to 0.080. All coordinate shifts were finally less than 5×10^{-4} A. No significant anisotropy was apparent for any atom when two further cycles were computed with the isotropic restrictions lifted. Atomic scattering factors used were, for Cl, those calculated from the self-consistent field model with exchange and, for Tc, those calculated from the Thomas–Fermi–Dirac statistical model and corrected for anomalous dispersion.[10] Final isotropic atomic parameters are listed in Table I, with the corre-

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TABLE I

ATOMIC PARAMETERS FOR THE $TcCl_4$ UNIT[a]

	x	y	z	B, A^2
Tc(1)	0.6282	0.1791	0.3984	1.26
Cl(2)	0.7430	0.3081	0.5739	1.50
Cl(3)	0.5125	0.3081	0.2239	1.63
Cl(4)	0.7462	0.0709	0.5474	2.25
Cl(5)	0.5101	0.0700	0.2502	2.25

[a] Atoms labeled as in Figure 1.

sponding structure factors for observed reflections in Table II. Bond lengths and angles are given in Table III. It was considered that realistic values for coordinate standard errors would be 1.5 times those indicated by the least-squares refinement. The standard errors in Tc–Cl bond lengths are then 0.006–0.007 A, and standard errors in bond angles subtended at the technetium atoms are 0.3°.

Discussion

The Crystal Structure.—The structure consists of chain polymers of composition $(TcCl_4)_n$, packed so that, when viewed end-on, the chain centers are approximately at the sites of a close-packed layer of spheres. The chains are extended parallel to the *c* axis, which corresponds to the longest morphological axis though it is the shortest crystallographically. That the crystals split lengthwise into bundles of fibers when attempts are made to cut them is easily understood in view of this structure. The interpolymer Cl···Cl contacts range from 3.56 to 3.80 A, which may all be considered normal van der Waals distances. (Pauling[11] quotes 1.80 A for the chlorine van der Waals radius.)

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

H	K	|FO|	|FC|
		L=0	
0	4	463	385-
0	6	825	837
0	8	2091	2211-
0	10	557	566
0	12	581	509
0	14	415	422-
2	0	75	73-
2	5	694	726
2	7	1086	1157-
2	9	621	703
2	13	534	555-
2	15	546	514
2	17	151	175-
2	19	206	196-
4	0	679	610
4	8	242	237-
4	12	278	323-
4	14	697	714
4	18	258	315-
6	0	78	79
6	1	614	649
6	5	582	650-
8	0	1935	1894
8	1	210	226-
8	4	165	211-
10	0	217	229-
10	1	927	954-
10	5	255	330
12	1	28	46
12	4	98	90
14	1	151	132
14	5	256	291-
		L=1	
0	2	909	804-
0	4	155	161
0	6	267	273-
0	8	180	206-
0	10	619	585
0	12	87	103-
0	14	56	59-
1	1	438	407
1	2	812	753-
1	3	789	815-
1	4	165	148-
1	5	591	593
1	6	147	179-
1	7	54	46-
1	8	160	179-
1	9	439	399-
1	10	639	583
1	11	454	446
1	13	188	190-
1	14	108	137-
1	15	88	97-
1	16	141	181
1	17	214	234
2	1	388	408-
2	4	1265	1290-
2	5	504	492-
2	6	264	234
2	8	75	54
2	9	453	424
2	11	412	425-
2	12	510	578
2	13	129	137
2	14	225	228-
2	15	95	121
2	17	246	254-
2	19	146	168
3	1	350	333-
3	2	506	496-
3	8	211	254-
3	9	341	399
3	10	214	314
3	11	288	387-
3	12	558	633-
3	14	152	168
3	15	155	146
3	16	194	211
3	17	225	250-
3	18	158	147-
3	19	154	154
4	2	470	490
4	3	241	229-
4	10	341	358-
4	12	472	514
4	13	120	127-
4	16	226	224-
4	18	163	173
5	1	239	218-
5	2	464	483
5	3	602	570
5	4	1183	1257-
6	1	211	210
6	2	61	64-
6	3	681	708-
6	4	681	716-
7	1	274	269
7	2	347	372
7	3	681	699-
7	4	92	99
8	1	81	89-
8	2	410	439-
8	3	134	132-
8	4	225	233
8	5	137	193
9	1	169	176
9	2	372	439-
9	3	220	277-
9	4	106	108
9	5	183	181
10	1	245	230-
10	3	181	264
10	4	475	576-
10	5	120	141-
11	1	180	186-
11	2	199	210-
11	3	217	301
11	4	552	584
11	5	169	190-
12	2	203	220
12	3	230	268-
12	4	360	397-
12	5	218	292
13	1	70	75-
13	2	243	245
13	3	241	259
13	4	514	539-
13	5	181	231-
14	3	308	337-
14	4	125	142-
14	5	274	308
15	3	301	344-
15	5	239	298
		L=2	
0	0	145	127
0	0	157	127
0	2	179	167-
0	4	84	83-
0	6	273	251
0	8	96	96-
0	12	124	129
0	14	180	164-
1	0	247	225-
1	1	669	619-
1	2	486	427
1	3	102	121
1	4	162	162
1	5	433	422
1	6	617	646-
1	7	506	557-
1	8	175	192
1	9	239	265
1	11	131	141
1	12	265	269-
1	13	351	355-
1	14	414	409
1	15	267	269
2	0	1664	1585-
2	1	319	273-
2	3	96	96
2	4	74	73
2	5	222	209
2	6	217	207
2	7	241	252-
2	8	889	903
2	9	97	115
2	10	194	220-
2	12	91	85-
2	13	162	161-
2	14	165	157-
2	15	96	126
2	16	324	364-
2	18	154	196
3	0	1417	1327-
3	1	858	857
3	2	602	556
3	3	280	245-
3	4	165	159
3	5	505	489-
3	6	483	546-
3	7	654	721
3	8	756	839
3	9	382	420-
3	10	223	244-
3	12	263	249-
3	13	367	375
3	14	306	309
3	15	302	347-
3	16	284	330-
4	0	534	506-
4	1	245	223
4	2	276	253
4	4	57	54
4	6	264	265-
4	7	190	121
4	8	298	334
4	9	128	165-
4	10	110	95-
5	0	1324	1303
5	1	750	742
5	2	592	603-
5	3	196	194-
5	4	162	155-
5	5	366	368-
6	0	985	955-
6	1	359	366
6	5	122	119-
7	0	178	189
7	1	585	618-
7	2	254	280-
7	3	97	124
7	4	99	90-
7	5	328	355
8	0	178	167
8	1	209	217
8	2	109	118-
8	5	92	85
9	0	237	235-
9	1	200	225-
9	2	255	262
9	4	111	115
9	5	183	210
10	0	635	603-
10	3	89	72
10	5	125	140
11	0	447	491-
11	1	409	394
11	2	202	204
11	3	112	117-
11	5	222	282-
12	0	143	144-
12	1	277	265
12	2	98	101
13	0	550	616
13	1	281	305
13	2	316	317-
13	5	138	136-
15	5	162	180
		L=3	
0	2	841	773-
0	4	2168	2141
0	6	616	621-
0	8	363	373-
0	10	471	511
0	12	1107	1065-
1	1	202	171-
1	2	93	85
1	3	435	390
1	4	537	510-
1	5	371	329-
1	6	57	74
1	7	82	76
1	8	132	130
1	9	150	150
1	10	61	68-
1	11	225	227-
1	12	232	244
1	13	139	149
2	1	488	413-
2	2	109	113
2	3	1115	1022
2	5	924	804-
2	6	96	79
2	9	572	521
2	11	701	628-
2	13	302	304
2	15	165	163
2	17	336	338-
3	1	45	44
3	2	332	318
3	3	147	120-
3	6	129	146
3	9	143	119-
3	10	261	255-
3	11	106	86
4	1	65	68
4	2	754	724
4	4	208	170
4	6	141	155
4	8	218	239
4	10	718	711-
4	14	236	225
4	16	246	260-
4	18	353	382
5	1	47	52
5	2	243	247-
6	1	386	392
6	3	558	568-
6	4	86	79
6	5	362	350
7	1	140	146-
7	3	257	272
7	4	244	260
7	5	200	218-
8	2	478	514-
8	3	139	155
8	4	1254	1303
8	5	122	151-
9	1	72	65-
9	2	95	120
9	3	189	205
9	4	381	372-
9	5	169	188-
10	1	230	195-
10	2	112	131
10	3	796	737
10	4	170	153-
10	5	658	662-
11	2	157	167
11	3	115	118-
12	1	85	91
12	2	340	343
13	2	95	97-
14	3	138	162-
		L=4	
0	0	238	231-
0	2	640	598
0	4	104	97
0	6	783	786-
0	8	148	167
0	10	107	112-
1	0	194	164
1	1	549	468-
1	2	202	183
1	3	173	158
1	5	271	234
1	6	346	332-
1	7	370	397-
1	8	87	119-
1	9	286	278
1	12	107	101-
1	13	184	171-
1	14	259	236
2	0	577	506
2	1	655	625
2	2	168	139-
2	3	189	188-
2	5	485	428-
2	7	548	585
2	8	360	367-
2	9	315	308-
2	10	187	154
2	13	385	366
2	15	300	310-
2	16	125	169
3	0	969	868-
3	1	147	129
3	2	315	276
3	4	88	76
3	5	186	163-
3	6	224	222-
3	7	148	157
3	8	631	623
3	10	219	205-
3	11	128	117-
3	12	159	125-
3	13	196	174
3	16	247	260-
4	0	1175	1139
4	1	183	145-
4	2	337	313-
4	4	204	180-
4	6	370	351
4	7	119	102-
4	8	768	810-
4	9	108	110
4	10	110	114
4	12	301	317
4	14	232	233-
4	16	306	326
5	0	729	731
5	1	188	176
5	2	217	212-
5	5	99	113-
6	0	307	278
6	1	628	647-
6	3	90	82
6	5	312	289
7	0	235	227-
7	1	443	454-
7	3	129	120
7	5	190	191
7	5	105	191
8	0	227	225-
8	1	72	63-
8	2	394	405
9	1	183	166-
9	2	176	183
9	3	94	79
10	0	292	296
10	1	269	278
10	2	139	119-
10	3	116	155-
10	5	304	299-
11	1	68	65
11	2	184	175
11	5	114	119-
12	2	166	166-
13	2	89	95-
14	5	114	120
		L=5	
1	1	181	154-
1	2	352	277
1	3	383	327
1	4	357	338-
1	5	218	210-
1	6	62	74
1	7	62	76-
1	8	200	212
1	9	313	274
1	10	359	290-
1	11	296	240-
1	12	200	165
2	2	101	98-
2	4	814	691-
2	10	167	148
2	12	382	392
2	14	155	149-
3	1	341	278
3	2	518	451
3	3	716	620-
3	4	582	530-
3	5	530	509
3	6	310	279
3	8	130	127
3	9	346	322-
3	10	374	377-
3	11	407	421
3	12	322	302
3	13	224	227-
4	3	115	77-
4	5	133	101
5	1	237	241
5	2	517	532-
5	3	578	538-
5	4	668	645
5	5	507	454
6	2	57	72-
6	4	572	560-
7	1	158	172-
7	2	203	221-
7	3	353	369
7	4	291	281
7	5	236	267-
8	3	156	127-
8	5	162	160
9	2	197	185
9	3	156	151
9	4	231	217-
10	4	348	257-
11	2	192	185
11	4	214	211-
11	5	297	278
12	5	141	148
13	4	398	400
13	5	217	201
14	4	160	190-
15	5	154	193-
		L=6	
0	0	1090	965-
0	2	454	380
0	6	360	368-
1	0	539	519
1	1	435	391
1	2	147	130-
1	3	156	129-
1	4	76	77-
1	5	206	184-
1	6	147	134
1	7	346	341
1	8	405	384-
2	0	25	28-
2	1	523	450
2	2	176	150-
2	3	104	96-
2	5	294	247-
2	6	138	152
2	7	492	412
2	9	280	264-
2	10	108	84
3	0	79	57
3	1	134	118-
3	2	248	223-
3	5	116	112
3	6	272	295
3	7	163	132-
3	11	91	105
3	13	152	140-
3	14	206	200-
4	0	74	20-
4	2	212	180-
4	4	105	81-
4	5	117	45
4	6	367	338
4	12	134	166
4	14	288	266-
5	2	174	163
5	5	117	98
6	0	66	70-
6	1	252	249-
6	2	98	86-
6	5	238	240
7	1	268	206
7	5	166	175-
8	2	284	281
9	2	166	160-
9	5	82	94-
10	5	142	145-
11	5	80	82
		L=7	
0	2	628	506
0	4	222	172-
1	1	101	84-
1	3	223	191
1	4	120	121
1	5	240	177-
2	1	244	211
2	2	55	55-
2	3	511	420-
2	4	127	106
2	5	350	317
2	9	336	284-
3	2	156	134
3	4	347	299-
3	5	119	78-
3	6	162	143
4	2	241	197-
4	4	695	636
4	6	138	118-
4	8	211	203-
4	10	230	191
4	12	395	355-
5	4	233	213
6	3	486	404
6	5	409	337-
7	3	208	191
7	4	177	164-
7	5	223	182-
8	4	193	163-
10	4	114	92
11	4	218	202-
12	4	343	326
		L=8	
2	0	319	283
2	1	138	127-
3	1	401	321-
3	2	245	204-
3	5	211	164
3	6	261	247
4	0	235	186-
4	2	191	150
4	6	185	161-

[a] Structure factors are scaled up by five, making $F(000) = 4440$.

TABLE III

INTERATOMIC DISTANCES AND ANGLES IN THE $(TcCl_4)_n$ POLYMER

Distance	Length, A	Angle	Value, deg
Tc(1)–Cl(4)	2.238	Cl(2)Tc(1)Cl(3)	86.5
Tc(1)–Cl(5)	2.246	Cl(3)Tc(1)Cl(5)	89.9
Tc(1)–Cl(2′)	2.377	Cl(2)Tc(1)Cl(4)	89.7
Tc(1)–Cl(3′)	2.388	Cl(4)Tc(1)Cl(5)	94.1
Tc(1)–Cl(2)	2.490	Cl(3′)Tc(1)Cl(2)	84.2
Tc(1)–Cl(3)	2.493	Cl(3′)Tc(1)Cl(3)	89.2
Cl(2′)···Cl(3)	3.27	Cl(3′)Tc(1)Cl(5)	91.9
Cl(2′)···Cl(4)	3.32	Cl(3′)Tc(1)Cl(4)	93.9
Cl(2′)···Cl(5)	3.38	Cl(2′)Tc(1)Cl(3)	84.3
Cl(2′)···Cl(2)	3.43	Cl(2′)Tc(1)Cl(2)	89.6
Cl(3′)···Cl(2)	3.27	Cl(2′)Tc(1)Cl(4)	92.1
Cl(3′)···Cl(5)	3.33	Cl(2′)Tc(1)Cl(5)	94.0
Cl(3′)···Cl(4)	3.38	Tc(1)Cl(3′)Tc(1′)	95.6
Cl(3′)···Cl(3)	3.43	Tc(1)Cl(2)Tc(1′)	95.9
Cl(4)···Cl(5)	3.28		
Cl(2)···Cl(4)	3.34		
Cl(3)···Cl(5)	3.35		
Cl(2)···Cl(3)	3.42		

The Polymeric Chains.—Figure 1 illustrates the nature of the polymeric structure. Successive $TcCl_6$ octahedra are glide plane related and hence mirror images of each other. The structural repeating unit of the chain has the composition Tc_2Cl_8 comprising two parallel, approximately planar $TcCl_4$ groups, Tc(1)Cl-(2, 3, 4, 5) and Tc(1′)Cl(2′, 3′, 4′, 5′). Half the chlorine atoms of the chain are used in pairs, Cl(2, 3′) and Cl(2′, 3), to bridge adjacent technetium atoms. The two nonbridging chlorines of each octahedral group are in *cis* relationship.

This structure is the first example of its kind. AB_4-

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(11) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

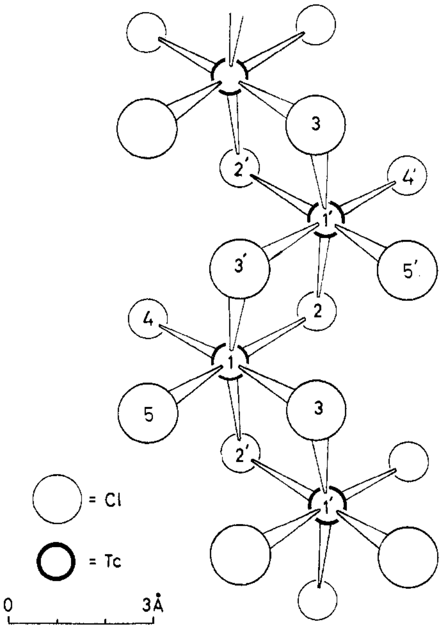

Figure 1.—A section of a $(TcCl_4)_n$ chain viewed normal to the *a* axis.

type structures, if they are not composed of discrete molecules, generally contain B atoms in closest packing[12] and can be described as three-dimensional networks of tetrahedra or octahedra. Two exceptions are the chain structure of NbI_4[13] and the layer structure of ThI_4[14] which has sheets of linked square antiprisms. In the NbI_4 structure, NbI_6 octahedra share opposite edges to form straight single chains rather than the zigzag chains of $TcCl_4$. Besides this difference there is another major distinction between NbI_4 and $TcCl_4$. Pairs of niobium atoms are displaced toward each other such that the Nb–Nb approach is 3.31 A, suggesting a metal–metal bond. The Tc–Tc length of 3.62 A seems to preclude such a bond, and the technetium atoms are actually displaced away from each other in the sense that the internal angle Cl(2)Tc(1)Cl(3′) is only 84°.

Dimensions of the Polymer.—There are three chemically distinct Tc–Cl bonds in the polymer and two crystallographically independent examples of each. The agreement within each pair is within 2σ so we shall consider the mean value of each chemical type. The shortest bonds (2.24 A) involve the nonbridging chlorine atoms Cl(4) and Cl(5). The longest bonds (2.49 A) are to bridging chlorines Cl(2) and Cl(3) aligned perpendicularly to the chain length. Intermediate in length (2.38 A) is the third pair of bonds to bridging chlorines Cl(2′) and Cl(3′) parallel to the chain length. The differences in length between these three types are highly significant, the smallest difference (0.11 A) being 15σ. All bond angles are within 6° of the 90° that would be expected for a regular octahedron. The angle of 94° between the two short bonds will reduce electrostatic repulsions between the two chlorines, and there is a correspondingly reduced angle of 86.5° between the two longest Tc–Cl bonds. Deviations from the least-squares plane through Tc(1) and Cl(2, 3, 4, 5) can be described in terms of a displacement of the bridging chlorines by 0.14 A on either side of the plane, in the directions of the neighboring technetium atom to which they bond. The interchlorine distance Cl(2)···Cl(3′) is thus reduced to 3.27 A, the shortest nonbonding distance in the polymer. The average of all of the intrapolymer Cl···Cl contacts is 3.35 A, or 0.25 A less than the van der Waals distance. It is clear that the resulting nonbonded repulsive forces are more than balanced by the strong bonding forces throughout the chain.

We shall consider the possibility of accounting for the variation in length of Tc–Cl bonds in terms of varying π-bond order. Technetium(IV) possesses the $4d^3$ configuration, and the magnetic properties of the compound indicate a spin-free $t_{2g}{}^3$ state. A simple bonding description is therefore in terms of σ-bond formation by means of octahedrally directed d^2sp^3 hybrid orbitals from Tc. There is, however, the further possibility of π-bond formation by overlap of suitably directed vacant 3d orbitals of the chlorines with the three singly occupied d orbitals of Tc, the d_{xy}, d_{yz}, and d_{xz}.

We shall choose the *z* axis to be parallel to the polymer chain so that chlorine atoms 2, 3, 4, and 5, with Tc(1), comprise the *xy* plane. It is clear that the singly occupied Tc d_{xy} orbital can overlap equally with 3d orbitals of the four chlorine atoms in the plane. If *y* is aligned along Tc(1)–Cl(3), the d_{yz} orbital could π bond equally with Cl(4) and Cl(3′) but to a reduced extent with Cl(2′) and Cl(3), since one lobe of the d_{yz} orbital lies in the tightly packed Tc_2Cl_2 ring where d-orbital overlap would be less likely for steric reasons. Similar considerations apply to the Tc d_{xz} orbital which could only π bond fully with Cl(5) and Cl(2′). These observations are summarized in Table IV. Assuming that the degree of overlap is zero within the Tc_2Cl_2 rings, the figures can be regarded as having the units of electrons. These figures have no quantitative basis but the relative degree of π bonding they predict is exactly in agreement with that indicated by the corresponding Tc–Cl bond lengths. Although steric effects may also influence the lengths of these bonds, the differences are so large as to support the tentative conclusion reached above that π-bond order is greatest with the nonbridging chlorines and least with those in *trans* relation to them.

TABLE IV

DEGREE OF π BONDING OF TECHNETIUM 4d ORBITALS WITH INDIVIDUAL CHLORINE ATOMS, PREDICTED FROM GEOMETRICAL CONSIDERATIONS

	Cl(4)	Cl(5)	Cl(2′)	Cl(3′)	Cl(2)	Cl(3)
d_{xy}	$^1/_4$	$^1/_4$			$^1/_4$	$^1/_4$
d_{yz}	$^1/_2$			$^1/_2$		
d_{xz}		$^1/_2$	$^1/_2$			
Total	$^3/_4$	$^3/_4$	$^1/_2$	$^1/_2$	$^1/_4$	$^1/_4$

Because our knowledge of π-bond order is only approximate, it is not possible to deduce a σ covalent

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[14] A. Zalkin, J. D. Forrester, and D. H. Templeton, *Inorg. Chem.*, **3**, 639 (1964).

radius for Tc(IV) from this structure. An upper limit would be 1.50 A, based on the long bonds Tc(1)–Cl(2) and Tc(1)–Cl(3). The only other reported Tc–Cl bond length is 2.35 A for the $Tc_2Cl_8^{3-}$ ion,[15] in which the oxidation state of Tc is V or VI.

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The Crystal and Molecular Structure of Bis(2,2,6,6-tetramethylheptane-3,5-dionato)nickel(II)

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The crystal and molecular structures of bis(2,2,6,6-tetramethylheptane-3,5-dionato)nickel(II), also called bis(dipivaloylmethanido)nickel(II), $Ni(DPM)_2$, have been determined in a single crystal X-ray diffraction study. The unit cell is monoclinic (space group $P2_1/a$) with dimensions $a = 10.70 \pm 0.01$ A, $b = 10.98 \pm 0.02$ A, $c = 10.39 \pm 0.02$ A, $\beta = 113° 16' \pm 15'$, and contains two formula units. As expected from earlier studies by Cotton and Fackler, the molecules are mononuclear, essentially planar, and centrosymmetric. The Ni-O distances, 1.836 ± 0.005 A, are much shorter than those in a number of complexes in which Ni(II) is octahedrally coordinated by oxygen atoms. This may be explained by the absence of electrons in the antibonding σ-MO with d_{xy} symmetry. The orientation of the molecules in the unit cell is fully described for future reference in the reporting of polarized optical absorption studies of this substance and its isomorphous Cu(II) analog.

Introduction

Studies of β-ketoenolate complexes of nickel(II) and cobalt(II) have established that while the acetylacetonates readily form polymeric structures by sharing of oxygen atoms,[1–5] the replacement of the methyl groups by larger groups leads to partial[2,3] or complete[2,3,6,7] dissociation, exclusively monomeric molecules being obtained when the methyl groups are replaced by the very bulky *t*-butyl group. Spectroscopic studies of the nickel[2] and cobalt[4,6] monomeric complexes of 2,2,6,6-tetramethylheptane-3,5-dionato ion lead to the conclusion that these were, respectively, square and tetrahedral, and, for the cobalt complex, this has been conclusively demonstrated by single crystal X-ray diffraction study.[6,7] The present paper reports an X-ray study which proves conclusively the planar structure of the nickel complex.

This study was undertaken not only to confirm this point but to provide knowledge of the orientation of the molecules in the unit cell for this compound and its isomorphous Cu(II) analog, in order that esr and polarized electronic spectral studies of the crystals might be made. The results of the latter studies will be reported later. However, in anticipation, this paper will describe the molecular orientations more explicitly and in more detail than is customary in reports of crystal structure studies intended purely to elucidate molecular structures.

The ligand molecule, systematically named 2,2,6,6-tetramethylheptane-3,5-dione, has also the common name dipivaloylmethane, DPM, which has been often used in the past. Henceforth in this paper we shall use the latter name and its abbreviation.

Experimental Section

Bis(dipivaloylmethanido)nickel(II), $Ni(DPM)_2$, was prepared by the reaction of dipivaloylmethane (2,2,6,6-tetramethylheptane-3,5-dione) and nickel acetate.[2] The dipivaloylmethane was prepared by the method of Adams and Hauser.[8] The product of the reaction of dipivaloylmethane with nickelous acetate was a green solid, believed to be the dihydrate of bis(dipivaloylmethanido)nickel(II). Upon drying under vacuum at 100°, the green solid lost water and turned red. The red solid was sublimed at 120° under a pressure of approximately 0.02 mm. A small amount of a yellow-green paperlike solid remained after sublimation. Sublimations were repeated until no residue was observed. Melting point determinations (uncorrected) on thrice sublimed material gave 224.5–225.5° in open-tube determinations and 225.0° in closed-tube determinations. Analysis of the thrice sublimed sample gave 62.32% carbon and 8.92% hydro-

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