listed in Table 3. All have axes of approximately 7 Å and 9 Å with a c axis of 10, 20 or 40 Å depending upon whether there are 2, 4 or 8 molecules per unit cell, respectively. For those in monoclinic space groups, the β angle is never far from 90°.

L17 also has an axis of 7 Å but it is chemically quite different from the other compounds discussed above, and consequently its b and c axes are different.

The author is indebted to Mr R. G. Howells of the Department of Physics, University College, Cardiff, and to Professor D. Rogers of the Department of Chemical Crystallography, Imperial College, London for their advice, guidance and encouragement during the performance of this work.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

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The crystal structure of tris-(2-dimethylaminoethyl)amine nickel(II) and copper(II) bromides.

By M. DI VAIRA and P. L. ORIOLI, *Istituto di Chimica Generale e Inorganica, Università di Firenze, Florence, Italy*

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The crystal structures of $Ni(Me_6tren)Br_2$ and $Cu(Me_6tren)Br_2$ [$Me_6tren = N\{CH_2CH_2N(CH_3)_2\}_3$] have been determined by three-dimensional X-ray analysis and refined to final R values of 7·7% and 6·2% respectively. Crystals of the two complexes are cubic, space group $P2_13$, $a = 12{\cdot}123 \pm 0{\cdot}002$ and $a = 12{\cdot}137 \pm 0{\cdot}003$ Å for the nickel(II) and copper(II) compounds respectively, with four formula units per unit cell. The two structures consist of $M(Me_6tren)Br^+$ and Br^- ions arranged in a distorted NaCl type arrangement. The coordination polyhedron about the metal atoms is a trigonal bipyramid with C_3 crystallographic symmetry. The structure is essentially identical with that of the corresponding cobalt compound.

Ciampolini & Nardi (1966*a*,*b*) have reported the preparation and the chemical properties of a series of five-coordinated high-spin complexes with general formula

$$M^{II}(Me_6tren)X_2,$$

where M^{II} = Cr, Mn, Fe, Co, Ni, Cu, Zn and Me_6tren = tris-(2-dimethylaminoethyl)amine, $N\{CH_2CH_2N(CH_3)_2\}_3$ and X = Cl, Br, I, NO_3 and ClO_4.

As a part of an X-ray structural investigation on the isomorphous series of the complex bromides, we have already reported in detail the structure of the cobalt(II) complex (Di Vaira & Orioli, 1967). We wish now to report the results of the X-ray analysis of the nickel(II) and copper(II) complexes. Since the experimental procedure has closely followed the lines of the structure determination of the cobalt(II) analogue only some significant different points will be mentioned here.

Crystals of the two compounds, kindly supplied by Dr Ciampolini, are tetrahedral in shape and belong to the space group $P2_13$. Cell dimensions, determined from Weissenberg photographs with the NaCl rotation pattern superimposed, are: $a = 12{\cdot}123 \pm 0{\cdot}002$ Å for the nickel(II) complex and $a = 12{\cdot}137 \pm 0{\cdot}003$ Å for the copper(II) complex; $Z = 4$. For Cu $K\alpha$ radiation $\mu = 73{\cdot}8$ and 75·6 cm^{-1} for the nickel(II) and copper(II) complexes respectively. The crystals selected for data collection had the shape of regular tetrahedra with edge about 0·25 mm.

A total of 443 independent reflexions were measured for the nickel(II) compound and 540 for the copper(II) compound.

Initial parameters for the atoms were taken from the last isotropic least-squares cycle of the structure of the cobalt(II) complex. After a few cycles of least-squares refinement with anisotropic temperature factors the final R values were 0·077 and 0·062 for the nickel(II) and copper(II) complexes respectively. Reduction of the intensities, structure factor calculations and least-squares refinement were performed at the C.N.U.C.E. in Pisa with programs written or adapted for the IBM 7090 by Stewart (1964). Table 1 reports the

final atomic parameters and the temperature factors with their estimated standard deviations, as calculated from the diagonal terms of the inverse least squares matrix.

Although a detailed comparison of the results will be postponed until the structures of all the members of the series are known, a few points should be mentioned in this connexion.

As expected from the isomorphism with the cobalt(II) complex the structure of the two complexes consists of $M(Me_6tren)Br^+$ and Br^- ions arranged in a distorted NaCl type arrangement. In the complex cation the metal atom is five-coordinated, the ligands being distributed at the apices of a trigonal bipyramid with C_3 crystallographic symmetry. The symmetry of the coordination polyhedron alone is C_{3v}. In both cases the metal atom lies below the equatorial plane of the three nitrogen atoms, the perpendicular distances from this plane being 0·22 Å for the nickel(II) complex and 0·20 for the copper(II) one.

Bond lengths and angles in the cation with their estimated standard deviations are reported in Table 2. In the copper(II)

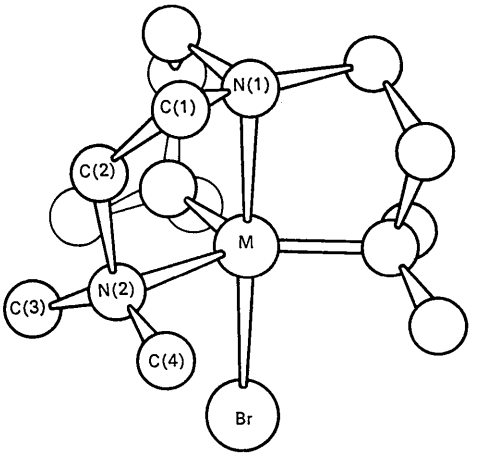

Fig. 1. A perspective drawing of the $M(Me_6tren)Br^+$ ion.

Table 1. *Positional parameters, temperature factors and their estimated standard deviations*

Anisotropic thermal factors are of the form: $\exp(-\sum_{i=1}^{3}\sum_{j=1}^{3} h_i h_j \beta_{ij})$.

Estimated standard deviations are given in parenthesis.

	Positional parameters × 10^4			Thermal parameters × 10^4					
	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
				$Ni(Me_6tren)Br_2$					
Ni	2320(2)	2320(2)	2320(2)	52(1)	52(1)	52(1)	−1(1)	−1(1)	−1(1)
Br(1)	1145(1)	1145(1)	1145(1)	54(1)	54(1)	54(1)	−8(1)	−8(1)	−8(1)
Br(2)	8169(1)	8169(1)	8169(1)	63(1)	63(1)	63(1)	4(1)	4(1)	4(1)
N(1)	3322(10)	3322(10)	3322(10)	50(10)	50(10)	50(10)	6(8)	6(8)	6(8)
N(2)	2752(11)	1052(11)	3463(10)	58(9)	38(9)	56(8)	2(9)	−16(7)	0(8)
C(1)	3633(12)	2663(13)	4321(12)	45(10)	48(10)	34(9)	15(8)	−5(8)	2(9)
C(2)	3771(12)	1476(11)	4015(12)	38(9)	48(8)	32(9)	5(8)	−26(9)	13(7)
C(3)	2946(14)	−32(15)	2959(14)	65(15)	45(13)	109(14)	31(10)	−2(11)	3(10)
C(4)	1868(16)	906(15)	4249(14)	50(12)	53(13)	80(11)	−17(11)	−12(11)	2(10)
				$Cu(Me_6tren)Br_2$					
Cu	2327(2)	2327(2)	2327(2)	53(1)	53(1)	53(1)	−3(1)	−3(1)	−3(1)
Br(1)	1189(2)	1189(2)	1189(2)	61(1)	61(1)	61(1)	−8(1)	−8(1)	−8(1)
Br(2)	8184(2)	8184(2)	8184(2)	70(1)	70(1)	70(1)	6(1)	6(1)	6(1)
N(1)	3311(11)	3311(11)	3311(11)	46(9)	46(9)	46(9)	11(7)	11(7)	11(7)
N(2)	2741(13)	1049(12)	3473(13)	55(10)	51(10)	62(10)	−7(9)	−10(9)	11(9)
C(1)	3604(16)	2676(14)	4298(16)	64(13)	45(10)	61(13)	−16(10)	7(11)	1(10)
C(2)	3759(14)	1459(14)	4033(13)	46(10)	53(11)	58(11)	0(9)	−10(9)	16(9)
C(3)	2961(17)	−64(12)	2977(19)	74(14)	31(8)	115(19)	15(9)	−17(14)	4(10)
C(4)	1872(13)	919(15)	4304(15)	42(9)	76(13)	60(11)	−14(10)	5(9)	25(10)

Table 2. *Distances and angles in the* $M^{II}(Me_6tren)Br^+$ *ion with their estimated standard deviations*

Primes refer to atoms related to reference atom by the threefold axis

	Distances (Å)			Angles (°)	
	M = Ni	M = Cu		M = Ni	M = Cu
M–Br(1)	2·467(2)	2·393(3)	N(1)–M–N(2)	84·2(5)	84·7(5)
M–N(1)	2·10(1)	2·07(1)	N(2)–M–Br(1)	95·8(3)	95·3(4)
M–N(2)	2·13(1)	2·14(1)	N(2)–M–N(2′)	119·0(5)	119·1(6)
N(1)–C(1)	1·50(2)	1·47(2)	M–N(1)–C(1)	107·7(9)	108(1)
C(1)–C(2)	1·49(2)	1·52(2)	C(1)–N(1)–C(1′)	111(1)	111(1)
C(2)–N(2)	1·50(2)	1·49(2)	N(1)–C(1)–C(2)	109(1)	111(1)
N(2)–C(3)	1·47(2)	1·50(2)	C(1)–C(2)–N(2)	110(1)	108(1)
N(2)–C(4)	1·44(2)	1·47(2)	C(2)–N(2)–C(3)	111(1)	109(1)
Br(1)–C(3)	3·41(2)	3·41(2)	C(2)–N(2)–C(4)	111(1)	108(1)
Br(1)–C(4)	3·87(2)	3·88(2)	C(3)–N(2)–C(4)	106(1)	108(1)
Br(1)–N(2)	3·42(1)	3·36(1)	M–N(2)–C(3)	114(1)	116(1)
N(2)–N(2′)	3·68(2)	3·70(2)	M–N(2)–C(4)	109(1)	111(1)
			M–N(2)–C(2)	104(1)	104(1)

Table 3. *Observed and calculated structure factors for* $Ni(Me_6tren)Br_2$

Columns are: H index, 10 F_o, 10$|F_c|$. Unobserved reflexions are marked by an asterisk; reflexions considered affected by extinction are marked by *E*.

	H,0,0			H,9,0			H,4,1		4	136*	36	10	255	286	4	240*	120	6	153*	86
									5	129*	91	11	200*	109	5	311	344	7	179	213
4	749	880	1	955E	1100	2	1060	1173	6	192	205	12	156	185	6	491	474			
6	239*	220	2	330	292	3	334	306	7	104*	73				7	242*	107		H,14,4	
8	323	364	3	330*	184	4	399	416	8	82*	87		H,10,2		8	235*	163			
10	434	455	4	343	302	5	845	838							9	332	333	4	182	187
12	342*	16	5	343*	39	6	542	485		H,14,1		3	397	390	10	199*	81			
14	298	310	6	348*	45	7	683	653				4	277*	200	11	179	182		H,5,5	
			7	368	304	8	510	471	2	125	114	5	379	357	12	192	229			
	H,1,0		8	347	282	9	290	272	3	120	100	6	279	231				5	242	208
			9	325*	23	10	278	260	4	226	251	7	303	288		H,10,3				
3	219	219	10	315	317	11	200	184	5	161	189	8	253*	193					H,6,5	
4	789E	1045	11	263	187	12	156	171	6	178	165	9	232*	47	3	380	433			
5	214*	10	12	204*	135	13	368	364				10	204*	66	4	414	406	5	346	336
6	241*	219				14	130	148		H,15,1		11	163*	146	5	248	214	6	536	537
7	601	713		H,10,0											6	240*	164	7	406	368
8	515	563					H,5,1		2	111	97		H,11,2		7	380	395	8	297	273
9	326	246	1	551	627				3	107	124				8	219*	111	9	236	201
10	340*	198	2	342*	90	2	270	262				3	314	351	9	255	234	10	222*	149
11	397	398	3	564	638	3	1071	1146		H,2,2		4	274*	127	10	221	208	11	244	292
12	347	298	4	354	260	4	1008	1020				5	285	239	11	133*	108	12	174*	70
13	314*	141	5	349*	69	5	879	900	3	823	946	6	260*	106				13	162	173
14	269*	19	6	346*	220	6	808	800	4	937	1037	7	246*	66		H,11,3				
			7	338*	147	7	741	707	5	336	313	8	227*	163	7	380	395		H,7,5	
	H,2,0		8	322*	64	8	315	271	6	1049	1185	9	212	192	8	219*	111	9	236	201
			9	333	232	9	397	390	7	368	375	10	166	143	9	255	234	10	222*	149
1	284	341	10	263*	192	10	238	270	8	417	444				4	253	266	5	336	317
3	173*	111	11	215*	51	11	275	253	9	266	191		H,12,2		5	238	265	6	326	350
4	419	517				12	148*	125	10	641	729				6	225*	189	7	234*	86
6	291	218		H,11,0		13	129*	101	11	282	284	3	290	309	7	233	246	8	507	507
7	274*	134				14	127	137	12	267*	151	4	262	287	8	197	195	9	248	264
8	300*	61	1	486	483				13	243*	218	5	272	287	9	172	133	10	211*	151
9	544	609	2	383	356		H,6,1		14	204*	135	6	266	269	10	133*	138	11	191	183
10	342*	91	3	396	361				15	142*	12	7	244	244				12	169	229
11	355	283	4	346*	38	2	630	655				8	189*	77		H,12,3				
12	339*	193	5	340*	1	3	1009	1028		H,3,2		9	153*	34					H,8,5	
13	310*	99	6	363	331	4	535	512							3	229*	177			
14	263*	52	7	314*	69	5	594	592	3	432	432		H,13,2		4	222*	65	5	272	282
			8	291*	27	6	145*	3	4	701	775				5	311	349	6	606	611
	H,3,0		9	259*	11	7	476	436	5	850	907	3	250	224	6	204	204	7	233*	161
			10	215*	129	8	503	463	6	652	699	4	275	296	7	183*	140	8	227*	106
1	687	823				9	164*	114	7	454	433	5	213*	109	8	209	228	9	215*	124
2	827E	1089		H,12,0		10	163*	119	8	612	648	6	195*	111	9	158	176	10	206	218
3	430	439				11	202	195	9	557	619	7	176*	24		H,13,3		11	169	191
4	481	568	1	341*	27	12	143	177	10	276*	240	8	170	168				12	123*	88
5	582	645	2	339*	234	13	118*	35	11	276*	118				3	203*	179		H,9,5	
6	1037E	1291	3	334*	225	14	84*	15	12	268	227		H,14,2		4	194*	78			
8	313	301	4	327*	201				13	236*	158				5	181*	59	5	340	338
9	560	581	5	491	518		H,7,1		14	195*	90	3	198	141	6	164*	159	6	409	369
10	345*	21	6	299*	188				15	126*	127	4	182*	95				7	282	271
11	348*	168	7	293	253	2	148	130				5	203	164		H,14,3		8	215*	109
12	380	340	8	246*	171	3	211	230		H,4,2		6	166	158				9	200	192
13	302*	145	9	234*	144	4	713	680							3	164*	169	10	172*	17
14	257	247				5	370	356	3	905E	1046		H,15,2					11	137*	96
				H,13,0		6	357	325	4	770	829					H,9,6				
	H,4,0					7	162	140	5	488	459	3	203	216					H,10,5	
			1	314*	122	8	196	207	6	267	288				4	1009	980			
1	571	645	2	315	230	9	224	200	7	562	543		H,3,3					5	365	384
2	686E	922	3	419	481	10	287	308	8	414	383					H,5,4		6	222*	6
3	515	561	4	291*	169	11	162	159	9	275	214	3	824	878				7	211*	72
5	575	516	5	275*	159	12	132	125	10	282	224				4	191	172	8	195*	81
6	272*	130	6	253*	53	13	106	117	11	462	507		H,4,3		5	432	382	9	175	185
7	296*	62	7	253	227				12	257*	200				6	526	490	10	141*	44
8	318*	161					H,8,1		13	227*	190	3	721	772	7	481	460			
10	416	439		H,14,0					14	182*	107	4	253	248	8	651	658		H,11,5	
11	421	421				2	685	738				5	328	286	9	383	392			
12	327*	180	1	269*	76	3	722	749		H,5,2		6	421	416	10	265	262	5	214*	104
13	342	356	2	263*	94	4	245	245				7	599	586	11	261	269	6	203*	175
14	241	251	3	253*	72	5	315	285	3	618	604	8	229*	18	12	206*	153	7	187*	178
			4	241	198	6	472	454	4	762	812	9	584	593	13	172*	47	8	169	183
	H,5,0		5	253	306	7	313	303	5	385	372	10	244*	110				9	137*	109
			6	182*	111	8	304	264	6	336	336	11	243	244		H,6,4				
1	923	1070				9	193	195	7	540	547	12	222*	88					H,12,5	
2	412	448		H,15,0		10	151*	79	8	301	277	13	194*	175	4	656	639			
3	390	457				11	136*	111	9	280	247				5	522	494	5	189*	36
4	265	216	1	201*	151	12	155	150	10	330	325		H,5,3		6	337	299	6	174*	123
5	944	1071	2	225	244	13	103	136	11	269*	150				7	367	376	7	267	301
6	471	461	3	175*	143				12	307	339	3	317	355	8	243*	142	8	125	126
7	315	288					H,9,1		13	217	210	4	182*	99	9	512	510			
8	329*	255		H,1,1					14	203	225	5	831	815	10	278	286		H,13,5	
9	349	260				2	331	321				6	314	288	11	219*	37			
10	349*	136	2	831	840	3	255	235		H,6,2		7	468	433	12	195	202	5	167	186
11	400	368	3	870	769	4	418	366				8	464	460	13	155	170			
12	371	365	4	386	383	5	318	296	3	489	456	9	364	352					H,6,6	
13	275*	93	5	774	835	6	349	348	4	501	530	10	286	242		H,7,4				
14	215*	168	6	598	619	7	164*	71	5	238	149	11	238	244				6	403	463
			7	1373	1423	8	379	339	6	712	741	12	217	194	4	418	411			
	H,6,0		8	389	403	9	306	307	7	523	542	13	181*	74	5	259	235		H,7,6	
			9	610	661	10	397	374	8	514	520				6	631	613			
1	659	744	10	161*	89	11	121*	95	9	363	376		H,6,3		7	409	364	6	200	193
2	252	233	11	164*	16	12	95*	51	10	312	281				8	244*	133	7	183*	71
3	263	237	12	208	205				11	296	291	3	671	695	9	290	283	8	211	236
4	299	268	13	205	200		H,10,1		12	275	286	4	521	496	10	227*	69	9	172*	98
5	560	556	14	126*	72				13	195*	107	5	605	578	11	217	242	10	157*	35
6	710	709	15	93*	72	2	162*	134	14	166	141	6	397	382	12	176	196	11	136*	173
7	324*	184				3	280	265				7	535	483	13	155	178			
8	726	799		H,2,1		4	228	218		H,7,2		8	407	406					H,8,6	
9	348*	29				5	375	353				9	244*	190		H,8,4				
10	346*	234	2	960	1037	6	536	487	3	269	267	10	240*	88				6	287	357
11	463	468	3	940	898	7	409	410	4	409	359	11	225*	154	4	666	698	7	180*	52
12	299*	113	4	348	331	8	440	458	5	773	826	12	204	193	5	449	444	8	173*	58
13	364	372	5	445	489	9	140*	87	6	261*	92	13	174	207	6	243*	174	9	199	244
			6	237	248	10	125	135	7	318	296				7	399	390	10	143*	54
	H,7,0		7	487	501	11	132	158	8	277*	151		H,7,3		8	264	254	11	151	234
			8	142*	41				9	628	622				9	244	264			
1	268*	86	9	625	669		H,11,1		10	303	286	3	692	786	10	216	222		H,9,6	
2	290	294	10	291	286				11	280	275	4	395	404	11	185*	157			
3	365	341	11	460	509	2	164*	57	12	244	260	5	598	622	12	150	156	6	178*	100
4	488	505	12	193	219	3	307	310	13	170*	50	6	246	247				7	266	327
5	498	493	13	290	309	4	365	379				7	282	291		H,9,4		8	163	207
6	513	521	14	189	229	5	223	210		H,8,2		8	349	312				9	145*	121
7	338*	192	15	183	192	6	155*	99				9	242*	202	4	266	299	10	125	156
8	407	341				7	150	135	3	468	429	10	281	307	5	290	307	11	88	151
9	348*	55		H,3,1		8	261	292	4	422	417	11	249	244	6	244*	124			
10	542	531				9	121*	52	5	265*	118	12	183*	55	7	240*	134		H,10,6	
11	314*	178	2	1285	1436	10	236	235	6	537	479				8	230*	210			
			3	1383	1481				7	620	607		H,8,3		9	214*	99	6	253	324
	H,8,0		4	1189	1240		H,12,1		8	277*	173				10	191*	93	7	160	225
			5	624	659				9	285	268	3	222*	86	11	238	262	8	143*	88
1	432	406	6	439	429	2	162	167	10	253*	153	4	492	496				9	144	197
2	300*	160	7	134*	76	3	265	258	11	231	200	5	545	534		H,10,4		10	91*	130
3	523	565	8	333	291	4	345	341	12	189*	32	6	245	239						
4	362	310	9	409	400	5	169	182				7	268	248	4	374	409		H,11,6	
5	329*	62	10	345	342	6	215	210		H,9,2		8	243*	116						
6	675	720	11	349	344	7	130*	75				9	235*	168		H,12,4		6	152	152
7	347*	15	12	266	268	8	155	179	3	440	433	10	222	189				7	200	294
8	703	755	13	171	191	9	95*	26	4	492	491	11	194*	88	8	147*	143	9	144	211
9	388	333	14	139	135				5	291	294	12	198	176						
10	322*	8	15	116	144		H,13,1		6	278*	71					H,13,4			H,12,6	
11	291*	110							7	276*	97		H,9,3							
12	250	219				2	238	287	8	285	248				4	185*	59	6	124*	57
						3	179	192	9	255*	131	3	277	289	5	172*	135			

complex, the average Cu–N distance of 2·10 Å and the N(2)–Cu–N(1) angle of 84·7° are in good agreement with the analogous values of the structure of

[(tren) (SCN)Cu]SCN

(2·07 Å and 84·1°; Jain & Lingafelter, 1967).

The value of the N(2)–Cu–N(1) angle is also in agreement with those found in several ethylenediamine metal chelates, and seems essentially imposed by the stereochemistry of the ligand.

For the nickel(II) complex there are no analogous structures available for comparison. The average Ni–N distance

Table 4. *Observed and calculated structure factors for* $Cu(Me_6tren)Br_2$

Columns are: K index, 10 F_o, 10$|F_c|$. Reflexions considered affected by extinction are marked by *E*.

	0,K,0			9,K,0		3	699	746	4	923	1023	4	451	446	9	318	312	6	106	98
						4	821	832	5	362	349	6	339	249	10	222	211	7	231	230
4	673E	852	1	311	308	5	824	819	6	1101	1219	7	330	332	11	157	156	9	169	213
8	381	442	2	546	568	6	737	666	7	328	319	8	181	195	12	88	172			
10	237	240	3	596	643	7	370	370	8	364	360	9	118	133					12,K,4	
14	231	215	4	230	199	8	280	264	9	184	159					10,K,3				
			5	197	187	9	287	261	10	692	766		12,K,2					5	141	147
	1,K,0		8	226	196	10	282	276	11	222	251				4	152	173	6	171	204
			10	215	195	11	227	265	12	148	162	3	262	282	5	266	232	7	129	134
3	757	754				12	149	144	13	150	175	4	157	129	7	308	281	8	173	179
4	504	537		10,K,0		14	135	120	14	165	173	5	343	335	8	148	128			
5	981	1011										6	192	186	9	111	100		13,K,4	
6	665	735	1	252	255		6,K,1			3,K,2		7	231	237	10	153	166			
7	166	127	4	354	327													6	114	143
8	313	306	6	282	273	2	312	303	3	418	426		13,K,2			11,K,3		7	84	126
9	1000	1103	7	565	529	3	296	302	4	884	1005									
10	588	646	9	372	351	4	538	500	5	718	729	3	126	122	4	332	317		14,K,4	
11	520	549				5	777	729	6	335	309	4	134	151	5	286	258			
				11,K,0		7	424	393	7	288	283	5	187	202	6	210	182	5	80	104
	2,K,1					8	454	453	8	414	397	6	115	114	7	208	191			
			1	328	348	9	318	312	9	336	366				9	197	217		5,K,5	
2	845E	1320	2	343	355	10	479	468	10	334	316		14,K,2		10	145	139			
3	955	1069	3	207	186	12	239	253	11	336	349							5	262	257
4	767	883	4	395	379	13	190	184	12	291	293	3	122	122		12,K,3				
5	517	551	5	349	297	14	137	137	13	225	227	5	171	176					6,K,5	
6	317	287	6	356	335				15	177	205	6	120	165	5	172	159			
7	224	210	7	203	200		7,K,1								6	144	151	5	355	335
11	277	273	8	119	124					4,K,2			15,K,2		8	132	130	6	517	479
12	274	235	9	106	120	2	523	504							9	132	148	7	252	246
15	204	213				3	213	183	3	728	800	3	84	109				8	599	580
				12,K,0		4	737	698	4	854	906					13,K,3		9	408	374
	3,K,0					5	345	322	5	805	788		3,K,3					11	157	182
			1	224	182	6	427	416	6	564	564				4	192	193	12	123	114
1	141	149	2	241	227	8	226	215	7	482	451	3	842	990	6	168	171			
2	224	203	3	299	294	10	420	408	8	458	452	4	722	765	7	139	110		7,K,5	
3	472	454	4	249	233	12	135	116	9	467	437	5	278	331						
4	440	404	5	333	337				10	216	206	6	726	722		14,K,3		5	393	383
5	382	409	6	122	111		8,K,1		12	137	142	7	708	726				6	402	386
6	248	256	7	179	204				13	231	256	9	361	339	4	107	130	8	204	189
7	463	450				3	299	275				10	359	379				9	266	252
8	521	526		13,K,0		4	400	370		5,K,2			238	254		4,K,4		11	141	180
9	232	226				5	291	282				12	129	140				12	190	210
10	656	698	1	166	189	6	447	426	3	801	832	13	150	156	4	927	915			
11	302	294	3	209	193	7	176	177	4	532	539	14	115	131	5	260	253		8,K,5	
12	214	213	4	272	263	8	239	234	5	379	385				6	567	551			
13	432	463	6	312	331	9	323	276	6	119	98		4,K,3		7	358	392	5	271	250
15	132	184				10	486	476	7	715	703				8	765	734	6	382	366
				14,K,0		11	288	271	9	359	345	4	255	247	9	257	258	7	466	444
	4,K,0					12	146	173	10	332	307	5	159	182	10	333	332	9	140	145
			3	286	294				11	235	204	6	522	510	12	271	313	11	159	178
1	456E	1116	4	164	164		9,K,1		12	299	284	7	377	394	14	96	122	12	96	118
3	438	458	5	178	196				13	163	176	8	437	450						
4	1517L	1772	6	97	124	2	673	718	14	153	154	10	423	417		5,K,4			9,K,5	
5	257	236				3	349	336				11	252	268						
6	427	434		1,K,1		4	272	259		6,K,2		12	167	149	5	395	368	5	297	286
7	420	407				5	339	289				13	101	110	6	509	472	6	257	269
8	333	300	3	678	735	6	209	175	3	720	707	14	106	102	7	203	202	7	220	220
9	249	229	4	410	426	7	234	199	4	351	351				8	390	366	9	148	147
12	280	242	5	734	813	8	222	245	5	423	411		5,K,3		9	354	365			
13	204	198	6	541	564	9	254	234	6	274	282				10	411	408		10,K,5	
			7	1112E	1132	10	154	140	8	500	467	4	229	266	11	244	257			
	5,K,0		8	389	412	11	115	103	10	294	256	5	744	748	13	118	125	5	376	392
			9	662	673				12	179	196	6	510	511				7	148	157
2	789	862	12	190	190		10,K,1		14	154	180	7	619	643		6,K,4		8	203	204
3	609	610	13	189	186							8	517	492						
4	408	408				2	162	182		7,K,2		9	393	382	5	429	434		11,K,5	
5	1094	1155		2,K,1		3	247	238				10	165	159	6	288	264			
6	550	552				4	276	284	3	482	486	11	277	277	7	620	590	6	240	252
7	584	593	2	899	1040	5	257	248	4	476	454	12	304	309	8	144	138	7	145	153
12	412	375	3	1263E	1514	7	220	199	5	522	529				8	148	138	8	130	127
13	212	206	4	954E	1139	9	383	377	6	429	437		6,K,3		10	225	228			
14	287	282	5	270	277	10	124	104	7	297	281				11	209	208		12,K,5	
			6	540	573	11	231	242	8	613	619	4	478	476	12	136	174			
	6,K,0		8	757	743				9	168	139	5	325	253				7	205	228
			9	272	279		11,K,1		10	290	251	6	356	331		7,K,4				
2	196	144	11	162	159				11	126	105	7	301	280					13,K,5	
3	1152	1242	12	206	208	2	468	470	12	261	240	8	242	254	5	450	396			
5	604	549	13	200	237	3	330	320				9	425	410	6	390	390	5	107	111
6	679	678	14	133	116	4	133	129		8,K,2		10	207	171	7	493	448	6	105	147
7	468	419				5	332	309				11	224	229	8	405	389			
8	699	642		3,K,1		6	231	199	3	648	668	12	181	175	10	314	319		6,K,6	
10	307	269				9	131	135	4	433	420	13	116	123	13	151	175			
11	352	326	2	838	838	10	151	149	5	326	307							6	476	478
12	122	138	3	1239E	1521				6	501	477		7,K,3			8,K,4				
13	127	138	4	345	305		12,K,1		7	203	151								7,K,6	
14	119	114	5	1087	1198				8	216	201	4	532	530	5	608	583			
			6	984	1000	2	173	202	9	284	256	5	463	471	7	202	167	6	272	249
	7,K,0		7	326	338	3	242	248	13	123	139	6	498	483	8	303	299	9	327	289
			8	710	740	6	203	194				7	186	185	9	142	120	11	249	300
1	594	638	9	194	185					9,K,2		8	324	275	10	132	134			
2	267	248	10	269	250		13,K,1					9	117	124	11	144	165		8,K,6	
3	1176	1167	11	283	253				3	566	558	10	409	408	12	146	181			
5	366	349	12	252	249	2	352	298	4	228	194	11	175	180				6	308	282
6	321	289	13	194	177	3	170	163	5	342	244	12	151	152		9,K,4		7	265	244
9	304	249	14	126	118	4	356	365	6	337	329	13	71	96				9	169	158
12	235	210				7	192	190	7	580	558				5	444	428			
13	152	143		4,K,1		8	84	115	8	338	313		8,K,3		6	461	454		9,K,6	
									9	186	154				7	364	368			
	8,K,0		2	387	376		14,K,1		10	158	78	5	416	396	8	250	229	8	172	166
			3	1154	1222							6	428	429	10	100	103	10	159	166
1	468	481	4	309	324	2	139	182		10,K		7	324	282	11	77	77	11	157	205
3	439	442	5	880	920	4	147	168				8	159	166						
4	205	183	6	566	596	5	185	171	3	235	231	9	185	183		10,K,4			10,K,6	
5	330	329	7	627	614				4	281	275	11	165	159						
6	746	752	8	319	316		15,K,1		5	328	288	12	147	158	5	353	334	6	362	341
7	314	274	9	334	331				6	323	316				6	242	218			
8	913	794	11	350	333	2	168	173	7	348	310		9,K,3		8	166	166		11,K,6	
9	335	295	12	338	331	3	86	103	9	259	244				10	119	124			
10	157	133	14	239	266				11	133	134	4	556	548	11	124	196	8	191	230
12	226	222					2,K,2					5	392	345						
				5,K,1						11,K,2		6	274	243		11,K,4				
			2	525	568	2	923E	1106				7	192	206						
						3	783	803	3	163	180	8	148	144	5	263	250			

of 2·11 Å is somewhat smaller than the value of 2·16 Å found in the octahedral Ni(tren) $(SCN)_2$ (Rasmussen, 1959).

In the case of copper(II) trigonal bipyramidal stereochemistries have already been found by X-ray analysis (Mori, Saito & Watanabe, 1961; Bertrand, 1967; Kilbourn & Dunitz, 1967; Jain & Lingafelter, 1967).

For nickel(II), the structure of a low spin trigonal bipyramidal complex has been recently published (Stevenson & Dahl, 1967). Ni(Me_6tren)Br_2 is the only case of this type of configuration so far reported for a high spin nickel(II) complex.

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The structure of poly-L-proline II.

By STRUTHER ARNOTT and S. DAVID DOVER, *Medical Research Council Biophysics Research Unit and Department of Biophysics, King's College, 26–29, Drury Lane, London, W. C.2, England*

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The crystal structure of poly-L-proline II (space group $P3_2$, $a=6{\cdot}62$, $c=9{\cdot}31$ Å (e.s.d.'s 0·01 Å) and three prolyl residues per unit cell) has been reappraised. Two crystal models have been considered: in the first the threefold helical molecules at each lattice point are all parallel; in the second there are two half coaxial antiparallel chains at each molecular site (such an arrangement corresponds to a statistical crystal structure in which each site is occupied, with equal probability, by up- and down-pointing chains). Refined molecular conformation and packing parameters have been obtained for both models by a least-squares method in which bond lengths and angles are constrained to have values in agreement with single-crystal analyses. The refined *non-statistical* model (with standard conformational angles $\varphi=99{\cdot}8°$, $\psi=-95{\cdot}1°$, $\omega=-0{\cdot}4°$) provides a markedly better fit with the X-ray intensities and is preferred also on stereochemical grounds.

Cowan & McGavin (1955) analysed the X-ray diffraction from doubly oriented films of poly-L-proline II and found a trigonal unit cell, space group $P3_2$, with $a=6{\cdot}62$, $c=9{\cdot}36$ Å (we find $a=6{\cdot}62$, $c=9{\cdot}31$ Å both with e.s.d. 0·01 Å). They concluded also that the three prolyl residues in each unit cell were in a single molecule related by the same left-handed screw triad as the space group. Sasisekharan (1959) published a similar molecular model and from consideration of intermolecular contacts and optical transforms decided the radius vector of one αC made an angle, ψ, between 30° and 35°, with **a**. Burge, Harrison & McGavin (1962) determined ψ to be $40\pm2°$ by examining the variation of R with ψ. A feature of both crystal models is a short (2·80 Å) γC···O contact between molecules which might be a CH···O hydrogen bond.

We have refined the crystal structure of poly-L-proline II using powder diffraction data and the linked-atom method of Arnott & Wonacott (1966*a*). In this method bond lengths and angles can be kept fixed at standard values while the variables are the chain dihedral angles (τ), the radius of αC (D) and the Eulerian angles ($\theta_x,\theta_y,\theta_z$) which determine the chain orientation. Additional parameters are the scale (K), the average isotropic temperature factor (B) and the molecular orientation (ψ). By those means the number and kind of variables is rendered appropriate to the paucity (only fifteen in this case) and low resolving power of intensity data given by the polymer.

The function minimized in a least-squares fashion was

$$\Theta=\Phi+\sum_h \lambda_h G_h \qquad (1)$$

where

$$\Phi=\sum_m \omega_m\{{}_oF_m-(1/K){}_cF_m \exp(-B\varrho^2/4)\}^2 \qquad (2)$$

and λ_h is the Lagrange multiplier appropriate to the constraint, $G_h=0$ to be imposed on the solution. Six equations, $G_h=0$, involving some of the cylindrical polar atomic coordinates with

$$G_1=R(1)-R(7)\,, \qquad G_2=\varphi(1)-\varphi(7)+120°\,,$$
$$G_3=Z(1)-Z(7)-c/3\,, \qquad G_4=R(4)-R(7a)\,,$$
$$G_5=Z(4)-Z(7a)-c/3\,, \qquad G_6=Z(5)-Z(8)-c/3\,,$$

were used so that all prolyl residues were joined appropriately in a left-handed threefold helix of pitch equal to c. (The atom numbering key is in Fig. 1.)

We have also considered another possible crystal model to determine if poly-L-proline has a statistical crystal structure like other polypeptides such as α-poly-L-alanine (Elliott & Malcolm, 1959; Arnott & Wonacott, 1966*b*) and β-poly-L-alanine (Arnott, Dover & Elliott, 1967). The second model has two half (coaxial) molecules at each lattice point, the half molecules having –CO.NH.CH= sequences of opposite sense. For such a model two more parameters are