Acta Cryst. (1968). B24, 683

The Crystal and Molecular Structure of Tris (thiourea) zinc (II) Sulphate

BY GIOVANNI DARIO ANDREETTI, LUIGI CAVALCA & AMOS MUSATTI
Istituto di Chimica Fisica, Università degli Studi, Parma, Italy

(*Received* 27 *July* 1967)

The crystal structure of $Zn[SC(NH_2)_2]_3SO_4$ has been determined by a three-dimensional X-ray analysis and refined by differential methods using anisotropic thermal parameters; final $R=0{\cdot}091$. Four formula units are contained in the orthorhombic ($Pca2_1$) unit cell: $a=11{\cdot}12_6$, $b=7{\cdot}77_3$, $c=15{\cdot}49_1$ Å. Zn coordinates to three S's from three thiourea molecules (Zn–S 2·33, 2·32 and 2·31 Å) and to one O from a sulphate group (Zn–O 1·98 Å), to form a tetrahedral arrangement. There are no significant differences between corresponding bond distances and angles in the three thiourea molecules, which are much the same as in the uncoordinated thiourea. Packing and hydrogen bonding are discussed.

Introduction

Thiourea-complexes of divalent metal sulphates have been prepared and preliminary examinations have been made by X-ray diffraction by Nardelli & Chierici (1958). Among these compounds, mono(thiourea) cadmium sulphate dihydrate, $Cdtu SO_4.2H_2O$, has been studied recently by a three-dimensional X-ray analysis which showed its crystal structure to be polymeric (Cavalca, Domiano, Fava Gasparri & Boldrini, 1967). In continuing this research, the crystal structure of tris(thiourea)zinc sulphate has been studied and the results of this analysis are reported in the present paper.

Experimental

Crystal data, refined by a least-squares procedure on powder diffractometer data, are as follows:

$Zn[SC(NH_2)_2]_3SO_4$, $M=389{\cdot}8$
$a=11{\cdot}126\pm0{\cdot}005$; $b=7{\cdot}773\pm0{\cdot}004$;
$c=15{\cdot}491\pm0{\cdot}005$ Å
$V=1339{\cdot}7$ Å^3, $Z=4$, $D_m=1{\cdot}923$, $D_x=1{\cdot}926$ g.cm^{-3}
$\mu=83$ cm^{-1} (Cu $K\alpha$)
$F(000)=792$
Space group $Pcam$ (D_{2h}^{11}) or $Pca2_1$ (C_{2v}^5) (from systematic absences).

Two series of equi-inclination Weissenberg photographs were taken at room temperature with use of the multiple-film technique and Ni-filtered copper radiation. The layers around [100] were collected with $h=0,1\ldots10$ and around [010] with $k=0,1\ldots6$. 1455 independent reflexions were observed out of a possible 1592. The intensities were measured photometrically and corrected for Lorentz, polarization and spot-shape factors. For the photographs taken around [100] the sample used was a roughly spherical fragment of mean radius 0·036 cm, and for the data taken around [010] a needle, with rectangular cross-section of mean radius 0·045 cm, was used. The absorption correction was calculated for the first set of data considering the sample as a sphere and for the second set assuming the sample to be a cylinder. The data of both zones were correlated and put on a common scale using the least-squares procedure of Rollett & Sparks (1960). The absolute scale was determined first by Wilson's method, then at the end of the refinement by comparison with the calculated values.

Table 1. *Final atomic fractional coordinates* ($\times10^4$), *thermal parameters* ($\times10$ Å^2) *with e.s.d.'s and ratios (e.s.d.)/(coordinate shift)*

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}	$\lvert r(x)\rvert$	$\lvert r(y)\rvert$	$\lvert r(z)\rvert$
Zn	637±2	1589±2	−6±1	32±1	33±1	23±1	0±1	0±1	0±1	10	3	20
S(1)	1268±3	3457±4	1685±2	26±1	26±1	17±1	0±2	1±2	0±1	15	10	∞
S(2)	2040±3	−18±5	−781±2	25±1	38±1	23±1	−5±2	−1±2	0±1	15	25	3
S(3)	−812±3	−26±5	688±2	26±1	34±2	24±1	5±2	0±2	0±1	4	5	10
S(4)	−213±3	3305±5	−1071±2	31±1	36±2	20±1	1±2	2±2	4±2	15	7	∞
O(1)	1540±9	3143±9	767±6	35±4	34±4	24±3	−3±5	1±6	−6±4	5	6	2
O(2)	1644±12	1948±16	2208±7	38±5	39±6	29±4	2±7	−2±7	3±6	7	5	7
O(3)	−9±12	3788±15	1796±7	34±4	40±5	32±5	3±7	−1±7	−2±5	4	40	4
O(4)	1976±9	4963±15	1960±7	32±3	33±4	27±4	−1±6	−1±5	−5±4	2	20	4
N(1)	1659±15	−1386±23	−2277±7	43±6	56±8	32±4	−10±8	−2±8	1±8	3	30	4
N(2)	−11±10	−1319±17	−1408±7	33±4	42±6	30±4	−8±7	−1±7	−3±5	2	2	4
N(3)	−711±13	−2464±17	1849±7	40±6	35±5	25±5	−4±7	2±8	−2±6	4	4	3
N(4)	1029±14	−2097±17	1106±12	34±5	28±6	42±9	8±11	5±11	2±7	40	3	5
N(5)	−2185±14	5050±28	−1150±9	40±6	50±10	30±5	7±9	−1±9	4±11	70	4	50
N(6)	−1494±16	4564±22	239±8	35±7	41±8	22±4	8±8	3±8	−3±8	8	3	3
C(1)	1151±12	−1009±19	−1538±7	31±5	33±6	21±4	2±6	−3±7	−4±7	3	4	3
C(2)	−87±12	−1656±18	1243±8	33±5	34±6	29±5	1±6	−4±8	0±8	4	16	1
C(3)	−1384±16	−4413±19	−598±9	36±7	25±5	23±5	4±7	3±9	3±8	6	5	5

Structure determination and refinement

From a piezoelectrical experiment the crystals were found to be non-centrosymmetric, and the $Pca2_1$ space group was chosen. From a three-dimensional Patterson synthesis the x,y coordinates for the Zn atom were obtained and a zero value was assigned to the z coordinate as there are no symmetry conditions limiting the choice of the origin along the z axis. Using the phases of the contributions of the zinc atom alone to the structure factors, a spurious mirror plane, running through the zinc atom perpendicular to [001], was introduced in the first Fourier calculation. Nevertheless, it was easy to find two enantiomorphous tetrahedral distributions of peaks around the zinc atoms which could be attributed to four sulphur atoms. Choosing one of these distributions, a starting series of coordinates for the heaviest atoms was obtained which gave a residual error index of $R=0{\cdot}28$. Successive Fourier syntheses led to the location of all the other non-hydrogen atoms. At this point, the refinement was continued by using Booth's differential synthesis, first with two isotropic cycles and then with four anisotropic cycles; the final values of the residual error index were $R=0{\cdot}091$, $R'=0{\cdot}099$ (R for observed reflexions only, R' considering also the unobserved reflexions, assuming $F_o=\frac{1}{2}F_{\min}$ when $F_c \geq F_{\min}$; multiplicities not considered).

Table 2. *Atomic peak heights* (e.Å^{-3}), *curvatures* (e.Å^{-5}) *and e.s.d.'s*

		ϱ	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	A_{kl}	A_{hl}	A_{hk}
Zn	obs.	73·4	696	700	761	−8	−4	−2
	calc.	73·3	702	703	754	−7	−5	−2
S(1)	obs.	39·9	390	400	431	5	8	1
	calc.	39·8	391	400	427	5	6	2
S(2)	obs.	36·2	377	329	375	−18	−13	−2
	calc.	36·1	374	336	371	−10	−12	−3
S(3)	obs.	36·4	370	339	371	25	−11	7
	calc.	36·3	368	344	372	19	−10	7
S(4)	obs.	35·5	340	325	382	−5	19	19
	calc.	35·5	341	331	376	−8	18	12
O(1)	obs.	13·9	115	134	110	−12	−11	−19
	calc.	13·7	117	135	107	−10	−12	−18
O(2)	obs.	12·6	95	89	105	−5	4	−6
	calc.	12·2	96	89	105	−7	4	−7
O(3)	obs.	12·5	87	109	116	10	−1	−4
	calc.	12·5	87	109	114	9	−1	−4
O(4)	obs.	13·4	116	108	124	3	0	1
	calc.	13·6	117	108	123	4	1	3
N(1)	obs.	9·6	75	68	97	−8	1	4
	calc.	9·5	75	71	96	−5	1	4
N(2)	obs.	10·6	101	83	95	−8	−2	−4
	calc.	10·7	103	88	97	−6	−1	−3
N(3)	obs.	11·2	87	94	115	10	−7	−9
	calc.	11·0	90	94	114	4	−8	−9
N(4)	obs.	10·5	85	113	79	10	4	5
	calc.	10·8	87	118	82	7	4	5
N(5)	obs.	9·7	79	66	86	5	−5	6
	calc.	9·6	79	70	86	5	−4	4
N(6)	obs.	10·7	84	82	100	−7	8	14
	calc.	10·5	85	85	99	−7	7	11
C(1)	obs.	9·8	84	82	95	−3	−10	−1
	calc.	9·7	85	83	95	−3	−9	−1
C(2)	obs.	9·1	86	84	92	−2	−4	−2
	calc.	9·3	85	83	89	−3	−3	−2
C(3)	obs.	9·8	73	91	92	0	6	4
	calc.	9·6	74	91	89	0	6	3
	e.s.d.	0·5	5	6	5	3	3	3

Table 3. *Observed and calculated structure factors*

A minus sign for F_o means 'less than'.

h	k	l	$10F_o$	$10F_c$	α	h	k	l	$10F_o$	$10F_c$	α	h	k	l	$10F_o$	$10F_c$	α	h	k	l	$10F_o$	$10F_c$	α	h	k	l	$10F_o$	$10F_c$	α
0	1	0	588	507	0	1	1	1	1107	1129	101	1	2	12	177	134	48	2	4	5	481	470	284	2	0	17	346	333	23	3	7	9	165	178	104
0	2	0	81	86	0	1	2	1	510	413	268	1	3	12	124	111	192	2	5	5	214	205	9	2	1	17	91	81	353	3	8	9	105	85	281
0	3	0	201	194	180	1	3	1	631	568	151	1	4	12	105	98	257	2	6	5	563	606	51	2	2	17	189	192	286	3	1	10	405	372	143
0	4	0	175	168	180	1	4	1	178	148	254	1	5	12	257	243	15	2	7	5	89	71	83	2	3	17	253	263	324	3	2	10	546	551	191
0	5	0	409	354	0	1	5	1	678	696	291	1	6	12	44-	23	298	2	8	5	141	146	83	2	4	17	225	236	290	3	3	10	87	74	169
0	6	0	1060	1292	0	1	6	1	170	152	256	1	7	12	141	121	155	2	9	5	142	125	321	2	5	17	97	144	2	3	4	10	362	357	3
0	7	0	290	255	0	1	7	1	384	361	79	1	8	12	16-	12	48	2	0	6	929	939	15	2	0	18	429	405	36	3	5	10	217	210	348
0	8	0	190	144	0	1	8	1	114	90	63	1	1	13	352	307	84	2	1	6	630	610	25	2	1	18	129	111	43	3	6	10	144	157	15
0	9	0	192	172	0	1	9	1	102	74	126	1	2	13	423	417	67	2	2	6	243	181	234	2	2	18	96	79	103	3	7	10	37-	22	130
0	10	0	67-	71	180	1	10	1	28-	33	313	1	3	13	184	164	211	2	3	6	673	758	127	2	3	18	150	132	62	3	8	10	178	178	204
0	0	2	877	1082	26	1	1	2	708	659	266	1	4	13	350	328	272	2	4	6	296	293	220	2	4	18	29	54	123	3	1	11	271	243	69
0	1	2	737	997	341	1	2	2	710	702	154	1	5	13	170	166	267	2	5	6	232	234	6	2	0	19	170	174	115	3	2	11	168	160	98
0	2	2	776	847	309	1	3	2	159	120	246	1	6	13	57	51	173	2	6	6	193	171	15	2	1	19	177	171	24	3	3	11	68	64	61
0	3	2	249	179	140	1	4	2	355	282	265	1	7	13	124	105	101	2	7	6	259	242	20	2	2	19	152	163	330	3	4	11	261	264	237
0	4	2	171	139	47	1	5	2	378	343	33	1	1	14	205	183	228	2	8	6	72	77	21	3	1	0	805	804	180	3	5	11	116	109	283
0	5	2	484	475	41	1	6	2	157	128	6	1	2	14	180	158	171	2	9	6	184	156	136	3	2	0	555	513	180	3	6	11	69	83	182
0	6	2	568	515	8	1	7	2	115	86	274	1	3	14	89	61	17	2	0	7	557	493	82	3	3	0	75	28	0	3	7	11	86	81	39
0	7	2	676	593	343	1	8	2	222	195	156	1	4	14	168	156	323	2	1	7	456	415	73	3	4	0	271	226	0	3	8	11	63	66	83
0	8	2	62	62	137	1	9	2	46-	30	270	1	5	14	183	177	68	2	2	7	153	142	190	3	5	0	516	553	0	3	1	12	510	505	184
0	9	2	80	51	235	1	10	2	48-	41	306	1	6	14	48	48	325	2	3	7	297	269	209	3	6	0	49-	18	180	3	2	12	205	185	141
0	10	2	16-	47	213	1	1	3	865	983	49	1	7	14	63	56	167	2	4	7	402	377	309	3	7	0	190	170	180	3	3	12	81	92	114
0	0	4	996	1122	246	1	2	3	1421	1733	95	1	1	15	227	214	178	2	5	7	166	172	80	3	8	0	207	220	180	3	4	12	175	190	328
0	1	4	846	1041	65	1	3	3	50-	17	94	1	2	15	468	456	95	2	6	7	255	246	131	3	9	0	170	157	180	3	5	12	332	353	6
0	2	4	288	205	151	1	4	3	799	810	266	1	3	15	49-	26	4	2	7	7	175	160	70	3	1	1	826	813	6	3	6	12	58	30	339
0	3	4	1162	1381	190	1	5	3	244	222	215	1	4	15	303	321	262	2	8	7	69	55	145	3	2	1	318	245	102	3	7	12	162	158	180
0	4	4	283	273	171	1	6	3	371	345	287	1	5	15	39-	10	236	2	9	7	31-	25	191	3	3	1	184	149	206	3	1	13	210	199	329
0	5	4	266	228	342	1	7	3	188	167	22	1	6	15	130	109	297	2	0	8	776	721	356	3	4	1	217	202	11	3	2	13	462	460	122
0	6	4	200	199	272	1	8	3	324	305	102	1	1	16	153	122	129	2	1	8	569	550	307	3	5	1	414	355	221	3	3	13	106	101	39
0	7	4	438	388	41	1	9	3	44	35	121	1	2	16	182	168	211	2	2	8	483	469	237	3	6	1	78	82	90	3	4	13	258	258	300
0	8	4	112	68	210	1	1	4	534	518	125	1	3	16	72	58	106	2	3	8	397	369	162	3	7	1	229	210	4	3	5	13	112	102	160
0	9	4	344	284	186	1	2	4	577	582	169	1	4	16	88	66	30	2	4	8	321	317	214	3	8	1	148	146	155	3	6	13	76	89	215
0	0	6	1012	1166	73	1	3	4	187	153	3	1	5	16	109	97	306	2	5	8	162	162	259	3	9	1	34-	11	26	3	7	13	68	78	330
0	1	6	637	648	226	1	4	4	335	279	341	1	6	16	11-	65	18	2	6	8	389	397	1	3	1	2	668	622	229	3	1	14	282	265	193
0	2	6	692	793	165	1	5	4	216	188	313	1	1	17	314	301	93	2	7	8	230	216	313	3	2	2	880	996	159	3	2	14	295	295	167
0	3	6	976	1145	169	1	6	4	111	102	120	1	2	17	136	114	31	2	8	8	150	141	233	3	3	2	249	204	215	3	3	14	55	41	235
0	4	6	953	1026	172	1	7	4	68	41	199	1	3	17	89	95	87	2	9	8	88	54	196	3	4	2	522	492	321	3	4	14	182	193	336
0	5	6	344	307	221	1	8	4	168	155	233	1	4	17	104	90	216	2	0	9	506	430	80	3	5	2	433	434	23	3	5	14	193	205	30
0	6	6	268	233	84	1	9	4	65	62	58	1	5	17	272	263	271	2	1	9	787	774	128	3	6	2	123	114	17	3	6	14	48	54	332
0	7	6	240	196	211	1	1	5	588	636	86	1	1	18	135	122	197	2	2	9	200	189	201	3	7	2	190	169	200	3	1	15	64-	11	5
0	8	6	86	85	115	1	2	5	796	926	100	1	2	18	56	37	104	2	3	9	689	784	248	3	8	2	264	287	162	3	2	15	92	66	61
0	9	6	341	266	167	1	3	5	488	466	35	1	3	18	35	36	177	2	4	9	278	269	156	3	9	2	65	58	229	3	3	15	40-	32	16
0	0	8	568	428	85	1	4	5	734	801	280	1	4	18	42	49	310	2	5	9	437	473	131	3	1	3	468	410	62	3	4	15	122	126	209
0	1	8	561	469	303	1	5	5	453	439	254	1	1	19	279	275	96	2	6	9	88	95	134	3	2	3	836	851	139	3	5	15	56	72	332
0	2	8	718	820	170	1	6	5	61	58	56	1	2	19	138	136	36	2	7	9	313	323	112	3	3	3	180	159	259	3	6	15	64	67	91
0	3	8	1204	1418	156	1	7	5	160	133	114	1	3	19	13-	16	288	2	8	9	124	114	182	3	4	3	473	453	345	3	1	16	284	283	152
0	4	8	659	739	190	1	8	5	248	223	105	2	0	0	922	1118	0	2	0	10	700	635	310	3	5	3	359	363	244	3	2	16	311	324	204
0	5	8	227	212	183	1	9	5	124	110	55	2	1	0	568	561	0	2	1	10	294	274	282	3	6	3	57	55	135	3	3	16	51	51	129
0	6	8	316	309	63	1	1	6	603	560	216	2	2	0	1074	1177	180	2	2	10	529	517	202	3	7	3	189	169	37	3	4	16	146	146	38
0	7	8	117	90	321	1	2	6	247	184	234	2	3	0	51-	61	180	2	3	10	450	442	261	3	8	3	55	70	124	3	5	16	106	123	322
0	8	8	237	219	173	1	3	6	135	111	133	2	4	0	858	894	180	2	4	10	395	386	203	3	9	3	74	75	97	3	1	17	186	195	150
0	9	8	325	253	158	1	4	6	206	166	47	2	5	0	141	130	0	2	5	10	255	258	277	3	1	4	838	888	157	3	2	17	153	137	38
0	0	10	996	987	327	1	5	6	330	307	356	2	6	0	314	267	0	2	6	10	222	219	323	3	2	4	809	794	180	3	3	17	40	38	146
0	1	10	360	314	93	1	6	6	111	90	232	2	7	0	154	131	0	2	7	10	126	122	297	3	3	4	120	88	246	3	4	17	66	81	203
0	2	10	483	443	152	1	7	6	136	102	211	2	8	0	75	66	180	2	8	10	157	138	222	3	4	4	393	384	8	3	1	18	181	176	182
0	3	10	639	674	225	1	8	6	54-	10	201	2	9	0	70	58	180	2	0	11	519	525	107	3	5	4	373	378	349	3	2	18	147	141	163
0	4	10	288	265	110	1	9	6	123	99	184	2	10	0	10-	132	180	2	1	11	561	523	177	3	6	4	117	116	44	3	3	18	78	85	152
0	5	10	222	224	82	1	1	7	676	692	149	2	0	1	845	922	119	2	2	11	350	309	177	3	7	4	197	178	196	3	1	19	205	209	48
0	6	10	433	447	330	1	2	7	638	667	32	2	1	1	1015	1217	28	2	3	11	46	51	248	3	8	4	234	202	204	3	2	19	18-	21	149
0	7	10	138	128	63	1	3	7	216	180	173	2	2	1	980	1016	297	2	4	11	326	369	206	3	9	4	56	48	108	4	0	0	479	370	180
0	8	10	104	104	240	1	4	7	365	346	225	2	3	1	464	393	264	2	5	11	193	183	165	3	1	5	171	118	353	4	1	0	67	47	180
0	0	12	902	872	4	1	5	7	492	503	319	2	4	1	654	601	288	2	6	11	283	300	105	3	2	5	600	604	62	4	2	0	244	162	0
0	1	12	501	473	350	1	6	7	100	100	183	2	5	1	153	114	358	2	7	11	169	129	143	3	3	5	154	158	90	4	3	0	57-	25	180
0	2	12	144	98	101	1	7	7	234	217	134	2	6	1	428	414	123	2	8	11	133	117	185	3	4	5	308	295	242	4	4	0	78	51	180
0	3	12	515	501	309	1	8	7	257	234	42	2	7	1	318	299	358	2	0	12	387	325	309	3	5	5	118	110	301	4	5	0	67	74	180
0	4	12	224	214	195	1	9	7	124	112	92	2	8	1	150	139	346	2	1	12	78	62	223	3	6	5	105	100	252	4	6	0	62-	37	0
0	5	12	219	217	354	1	1	8	186	120	33	2	9	1	128	117	257	2	2	12	204	181	233	3	7	5	96	99	245	4	7	0	86	67	0
0	6	12	437	458	329	1	2	8	392	369	160	2	0	2	744	764	28	2	3	12	491	509	214	3	8	5	242	263	69	4	8	0	63-	52	0
0	7	12	210	172	358	1	3	8	162	122	212	2	1	2	568	662	53	2	4	12	195	185	207	3	9	5	28-	16	151	4	9	0	109	126	180
0	8	12	105	116	31	1	4	8	333	324	329	2	2	2	751	722	114	2	5	12	57-	7	172	3	1	6	846	932	183	4	0	1	501	383	353
0	0	14	444	410	354	1	5	8	63-	57	76	2	3	2	738	766	177	2	6	12	227	225	286	3	2	6	294	281	192	4	1	1	509	379	220
0	1	14	828	900	336	1	6	8	98	102	300	2	4	2	564	523	120	2	7	12	61	48	273	3	3	6	128	119	75	4	2	1	639	607	275
0	2	14	336	296	329	1	7	8	39	45	127	2	5	2	497	521	89	2	0	13	668	618	106	3	4	6	312	302	17	4	3	1	1215	1428	259
0	3	14	380	342	165	1	8	8	175	162	155	2	6	2	385	373	1	2	1	13	159	130	114	3	5	6	451	491	349	4	4	1	680	764	291
0	4	14	192	174	308	1	9	8	62	45	266	2	7	2	217	186	58	2	2	13	306	263	282	3	6	6	86	76	275	4	5	1	118	105	252
0	5	14	353	312	346	1	1	9	510	456	98	2	8	2	196	184	105	2	3	13	378	385	202	3	7	6	222	207	171	4	6	1	48	32	274
0	6	14	259	226	359	1	2	9	590	585	102	2	9	2	117	109	191	2	4	13	278	286	291	3	8	6	89	79	186	4	7	1	86	72	166
0	7	14	356	404	346	1	3	9	61-	36	244	2	0	3	523	448	287	2	5	13	69	60	254	3	9	6	111	100	184	4	8	1	151	165	284
0	0	16	409	387	357	1	4	9	134	128	271	2	1	3	1003	986	39	2	6	13	240	252	135	3	1	7	372	328	137	4	9	1	222	249	260
0	1	16	320	276	322	1	5	9	248	250	251	2	2	3	895	964	330	2	7	13	98	89	44	3	2	7	141	131	38	4	0	2	1080	1110	268
0	2	16	57-	45	19	1	6	9	156	162	302	2	3	3	609	618	298	2	0	14	57-	24	223	3	3	7	120	126	263	4	1	2	327	265	16
0	3	16	262	242	195	1	7	9	192	177	73	2	4	3	467	424	347	2	1	14	230	219	14	3	4	7	106	140	245	4	2	2	438	371	149
0	4	16	93	86	66	1	8	9	231	179	74	2	5	3	416	401	15	2	2	14	141	119	65	3	5	7	108	125	65	4	3	2	594	641	281
0	5	16	252	233	312	1	9	9	5-	26	146	2	6	3	229	218	10	2	3	14	485	466	172	3	6	7	63	46	323	4	4	2	157	167	212
0	6	16	172-	179	1	1	1	10	332	262	132	2	7	3	371	332	65	2	4	14	108	104	146	3	7	7	109	81	116	4	5	2	66-	53	133
0	0	18	481	460	28	1	2	10	506	456	228	2	8	3	196	189	353	2	5	14	45-	20	8	3	8	7	48	59	129	4	6	2	415	455	282
0	1	18	93	65	175	1	3	10	156	120	143	2	9	3	232	217	280	2	6	14	55	48	44	3	9	7	85	80	307	4	7	2	158	151	138
0	2	18	344	301	186	1	4	10	251	238	36	2	0	4	455	358	115	2	7	14	115-	112	6	3	1	8	223	207	219	4	8	2	63-	19	276
0	3	18	195	177	120	1	5	10	62-	26	329	2	1	4	738	761	68	2	0	15	281	226	355	3	2	8	553	596	181	4	9	2	171	189	280
0	4	18	307	321	185	1	6	10	88	101	0	2	2	4	824	892	73	2	1	15	78	65	46	3	3	8	174	167	193	4	0	3	1114	1232	100
0	0	20	63-	68	150	1	7	10	87	80	110	2	3	4	475	452	186	2	2	15	230	224	336	3	4	8	426	460	355	4	1	3	147	126	60
1	1	0	838	698	180	1	8	10	129	117	221	2	4	4	589	551	80	2	3	15	362	373	277	3	5	8	248	274	7	4	2	3	547	492	286
1	2	0	220	135	0	1	1	11	825	823	54	2	5	4	289	271	53	2	4	15	46	55	298	3	6	8	169	183	336	4	3	3	721	836	268
1	3	0	414	327	0	1	2	11	374	317	126	2	6	4	262	249	63	2	5	15	69	59	297	3	7	8	88	93	162	4	4	3	346	345	251
1	4	0	91	92	180	1	3	11	308	252	95	2	7	4	276	237	39	2	6	15	109	90	23	3	8	8	227	223	163	4	5	3	66-	70	165
1	5	0	446	431	0	1	4	11	296	292	345	2	8	4	145	149	68	2	0	16	335	326	25	3	1	9	535	498	102	4	6	3	316	329	98
1	6	0	118	109	180	1	5	11	554	622	241	2	9	4	160	155	157	2	1	16	278	261	30	3	2	9	150	234	277	4	7	3	170	171	54
1	7	0	189	166	180	1	6	11	64	60	305	2	0	5	1011	1120	57	2	2	16	121	107	150	3	3	9	144	148	23	4	8	3	61-	51	292
1	8	0	63-	22	180	1	7	11	246	210	66	2	1	5	316	276	50	2	3	16	362	368	116	3	4	9	222	251	135	4	9	3	135	149	260
1	9	0	48-	64	180	1	8	11	202	164	133	2	2	5	469	417	354	2	4	16	117	116	132	3	5	9	326	341	284	4	0	4	742	696	220
1	10	0	19-	31	0	1	1	12	422	358	158	2	3	5	643	669	318	2	5	16	164	171	30	3	6	9	96	96	280	4	1	4	279	248	287

Table 3 (*cont.*)

h	k	l	$10F_o$	$10F_c$	α
4	2	4	384	343	257
4	3	4	318	282	310
4	4	4	223	241	282
4	5	4	91	89	307
4	6	4	184	183	208
4	7	4	144	157	235
4	8	4	86	82	285
4	9	4	38–	20	5
4	0	5	874	870	89
4	1	5	773	800	86
4	2	5	127	94	168
4	3	5	283	261	50
4	4	5	262	271	276
4	5	5	244	275	73
4	6	5	447	519	83
4	7	5	390	404	87
4	8	5	57–	45	194
4	9	5	34–	26	356
4	0	6	389	327	135
4	1	6	344	351	298
4	2	6	87	85	302
4	3	6	309	302	176
4	4	6	178	180	319
4	5	6	183	189	319
4	6	6	181	194	172
4	7	6	162	171	337
4	8	6	54–	23	275
4	9	6	87	90	163
4	0	7	1493	1641	74
4	1	7	780	793	83
4	2	7	219	210	112
4	3	7	290	276	304
4	4	7	135	154	62
4	5	7	217	337	90
4	6	7	497	599	80
4	7	7	291	328	91
4	8	7	118	129	71
4	9	7	18–	55	335
4	0	8	564	477	24
4	1	8	242	193	124
4	2	8	109	89	183
4	3	8	230	258	28
4	4	8	171	175	119
4	5	8	110	122	156
4	6	8	182	205	6
4	7	8	51	44	87
4	8	8	54	51	208
4	0	9	673	654	105
4	1	9	525	506	64
4	2	9	118	100	73
4	3	9	270	294	292
4	4	9	93	75	151
4	5	9	228	257	66
4	6	9	249	291	84
4	7	9	212	222	82
4	8	9	98	89	92
4	0	10	477	423	21
4	1	10	329	316	130
4	2	10	102	81	3
4	3	10	429	477	52
4	4	10	91	79	167
4	5	10	106	108	140
4	6	10	201	244	55
4	7	10	85	60	150
4	8	10	58	68	99
4	0	11	295	253	115
4	1	11	251	245	92
4	2	11	316	311	286
4	3	11	552	622	247
4	4	11	324	382	279
4	5	11	62	73	98
4	6	11	121	143	101
4	7	11	103	104	115
4	0	12	368	336	205
4	1	12	294	269	61
4	2	12	182	171	39
4	3	12	151	148	175
4	4	12	178	187	25
4	5	12	175	199	48
4	6	12	139	152	180
4	7	12	112	110	41
4	0	13	252	241	155
4	1	13	177	157	256
4	2	13	397	421	252
4	3	13	450	500	259
4	4	13	329	378	256
4	5	13	166	174	249
4	6	13	88	96	157
4	7	13	48	36	220
4	0	14	302	276	237
4	1	14	169	157	70
4	2	14	68–	14	61
4	3	14	129	144	238
4	4	14	48–	39	78
4	5	14	33	43	319
4	6	14	102	118	246
4	0	15	135	133	120
4	1	15	70–	44	181
4	2	15	372	394	242
4	3	15	294	342	269
4	4	15	330	381	249
4	5	15	80	83	226
4	6	15	14–	59	91
4	0	16	124	126	57
4	1	16	219	219	256
4	2	16	180	192	257
4	3	16	147	141	122
4	4	16	136	157	238
4	5	16	87	97	249
4	0	17	223	230	59
4	1	17	115	108	116
4	2	17	73	68	212
4	3	17	212	235	278
4	4	17	59	76	268
4	0	18	117	123	202
4	1	18	97	100	236
4	2	18	66	82	256
4	3	18	48	49	250
4	0	19	32–	303	79
4	1	19	21–	246	71
5	1	0	265	203	180
5	2	0	910	1032	180
5	3	0	292	282	180
5	4	0	674	750	0
5	5	0	57–	37	180
5	6	0	194	220	0
5	7	0	48–	11	0
5	8	0	244	283	180
5	9	0	48	81	180
5	1	1	134	60	236
5	2	1	515	481	238
5	3	1	165	148	288
5	4	1	401	400	40
5	5	1	267	275	138
5	6	1	98	95	101
5	7	1	128	126	326
5	8	1	122	148	233
5	9	1	72	68	273
5	1	2	628	578	167
5	2	2	459	411	189
5	3	2	254	234	148
5	4	2	476	505	3
5	5	2	321	326	343
5	6	2	57	27	39
5	7	2	216	223	179
5	8	2	116	126	201
5	9	2	55	66	175
5	1	3	421	384	305
5	2	3	260	224	229
5	3	3	84	20	35
5	4	3	217	223	59
5	5	3	186	183	239
5	6	3	51–	15	162
5	7	3	68	43	359
5	8	3	76	77	240
5	9	3	25–	24	100
5	1	4	746	762	191
5	2	4	171	167	173
5	3	4	206	206	216
5	4	4	152	139	332
5	5	4	451	494	24
5	6	4	158	185	327
5	7	4	248	252	195
5	8	4	118	125	139
5	9	4	78	89	203
5	1	5	464	417	245
5	2	5	65–	66	350
5	3	5	89	84	148
5	4	5	181	170	215
5	5	5	288	313	74
5	6	5	51–	26	148
5	7	5	178	194	238
5	8	5	50	62	36
5	9	5	18–	22	208
5	1	6	633	619	154
5	2	6	492	500	182
5	3	6	99	84	342
5	4	6	254	268	2
5	5	6	228	258	320
5	6	6	135	150	40
5	7	6	159	167	147
5	8	6	162	175	186
5	1	7	384	370	255
5	2	7	249	228	312
5	3	7	39	35	163
5	4	7	145	148	115
5	5	7	207	227	89
5	6	7	49–	12	48
5	7	7	99	99	249
5	8	7	66	86	222
5	1	8	438	433	174
5	2	8	429	443	209
5	3	8	117	104	156
5	4	8	254	296	47
5	5	8	374	436	339
5	6	8	66	62	39
5	7	8	118	128	173
5	8	8	130	138	216
5	1	9	94	79	63
5	2	9	433	446	268
5	3	9	62	81	260
5	4	9	249	263	100
5	5	9	64	57	343
5	6	9	91	93	76
5	7	9	88	84	111
5	8	9	168	188	272
5	1	10	321	299	212
5	2	10	484	510	134
5	3	10	102	99	272
5	4	10	279	308	327
5	5	10	228	251	22
5	6	10	39–	35	68
5	7	10	120	119	241
5	8	10	153–	148	143
5	1	11	75–	7	270
5	2	11	153	138	257
5	3	11	52–	9	248
5	4	11	92	87	37
5	5	11	67	83	93
5	6	11	31	35	196
5	7	11	76	80	212
5	1	12	262	270	236
5	2	12	440	458	170
5	3	12	50–	11	239
5	4	12	244	271	59
5	5	12	97	108	357
5	6	12	99	98	49
5	7	12	44	53	238
5	1	13	313	310	298
5	2	13	112	109	166
5	3	13	68	63	349
5	4	13	138	142	358
5	5	13	165	178	121
5	6	13	48	32	313
5	1	14	349	352	150
5	2	14	97	109	179
5	3	14	88	100	191
5	4	14	100	110	62
5	5	14	281	298	338
5	6	14	51	58	55
5	1	15	160	147	251
5	2	15	133	147	281
5	3	15	49	31	344
5	4	15	68	76	113
5	5	15	93	110	29
5	1	16	207	259	177
5	2	16	153	150	174
5	3	16	66	62	272
5	4	16	118	136	20
5	1	17	164	159	209
5	2	17	144	155	329
5	3	17	55	61	223
5	4	17	124–	135	159
5	1	18	44	46	118
5	2	18	228	268	192
6	0	0	145	125	0
6	1	0	720	720	180
6	2	0	187	140	180
6	3	0	222	228	0
6	4	0	260	277	180
6	5	0	227	283	180
6	6	0	93	91	180
6	7	0	206	192	180
6	8	0	109	120	180
6	9	0	31	54	0
6	0	1	391	330	52
6	1	1	572	534	70
6	2	1	397	380	114
6	3	1	533	554	310
6	4	1	136	134	113
6	5	1	331	389	48
6	6	1	163	161	53
6	7	1	271	312	87
6	8	1	68	62	69
6	9	1	106	117	310
6	0	2	859	802	202
6	1	2	670	672	214
6	2	2	128	101	299
6	3	2	473	490	325
6	4	2	229	255	318
6	5	2	274	287	207
6	6	2	307	347	199
6	7	2	156	168	212
6	8	2	86	96	223
6	9	2	127	157	304
6	0	3	1062	1070	76
6	1	3	419	372	13
6	2	3	483	443	316
6	3	3	116	117	327
6	4	3	434	470	305
6	5	3	258	275	5
6	6	3	306	321	76
6	7	3	124	135	5
6	8	3	88	84	337
6	9	3	18–	53	44
6	0	4	728	627	223
6	1	4	284	245	225
6	2	4	476	469	311
6	3	4	320	320	268
6	4	4	376	415	340
6	5	4	258	284	278
6	6	4	306	351	214
6	7	4	127	135	193
6	8	4	91	89	296
6	0	5	505	487	73
6	1	5	339	319	325
6	2	5	411	390	323
6	3	5	537	590	269
6	4	5	272	270	322
6	5	5	180	187	282
6	6	5	171	193	95
6	7	5	147	158	4
6	8	5	84	95	285
6	0	6	406	380	159
6	1	6	326	290	251
6	2	6	529	553	338
6	3	6	342	363	355
6	4	6	307	338	334
6	5	6	132	149	326
6	6	6	114	133	172
6	7	6	132	138	243
6	8	6	118	139	329
6	0	7	302	284	338
6	1	7	324	293	167
6	2	7	438	469	240
6	3	7	488	522	308
6	4	7	306	346	229
6	5	7	106	117	190
6	6	7	121	140	4
6	7	7	105	123	143
6	8	7	67	91	244
6	0	8	287	239	119
6	1	8	150	153	2
6	2	8	210	213	27
6	3	8	392	438	26
6	4	8	237	267	355
6	5	8	49	54	52
6	6	8	81	86	119
6	7	8	39–	18	71
6	8	8	74	78	18
6	0	9	399	357	137
6	1	9	272	258	149
6	2	9	259	254	227
6	3	9	261	270	208
6	4	9	301	334	248
6	5	9	130	121	172
6	6	9	128	140	110
6	7	9	76	94	185
6	0	10	202	194	132
6	1	10	312	300	127
6	2	10	282	296	55
6	3	10	387	438	359
6	4	10	287	329	63
6	5	10	177	215	103
6	6	10	51	53	103
6	7	10	141	138	135
6	0	11	563	555	160
6	1	11	389	404	62
6	2	11	195	199	144
6	3	11	414	445	222
6	4	11	88	84	152
6	5	11	106	122	80
6	6	11	262	293	156
6	7	11	166	160	82
6	0	12	380	360	160
6	1	12	262	282	150
6	2	12	327	353	80
6	3	12	253	273	357
6	4	12	124	108	44
6	5	12	134	150	134
6	6	12	168	172	165
6	0	13	372	350	77
6	1	13	244	248	93
6	2	13	74	56	191
6	3	13	114	99	342
6	4	13	85	80	147
6	5	13	135	152	85
6	6	13	162	184	71
6	0	14	324	322	170
6	1	14	124	126	182
6	2	14	69	62	183
6	3	14	82	87	153
6	4	14	94	102	23
6	5	14	88	87	166
6	0	15	408	483	74
6	1	15	82	64	358
6	2	15	97	110	328
6	3	15	129	145	20
6	4	15	136	160	307
6	5	15	34	32	10
6	0	16	276	286	173
6	1	16	202	218	216
6	2	16	142	133	282
6	3	16	65	66	342
6	4	16	61	59	255
6	0	17	118	117	328
6	1	17	180	188	36
6	2	17	67	79	311
6	3	17	188	240	290
6	0	18	78	103	197
6	1	18	144–	164	238
7	1	0	89	47	180
7	2	0	516	541	180
7	3	0	64	87	0
7	4	0	335	358	0
7	5	0	111	109	180
7	6	0	37	24	0
7	7	0	57	49	0
7	8	0	93	101	180
7	1	1	439	371	199
7	2	1	763	857	274
7	3	1	40–	34	183
7	4	1	365	393	98
7	5	1	254	303	68
7	6	1	116	114	128
7	7	1	50–	44	349
7	8	1	208	233	282
7	1	2	279	251	226
7	2	2	92	89	177
7	3	2	198	183	105
7	4	2	54	45	5
7	5	2	163	170	6
7	6	2	42	39	0
7	7	2	87	92	247
7	8	2	48	41	214
7	1	3	655	651	284
7	2	3	73	69	225
7	3	3	55	45	52
7	4	3	124	103	118
7	5	3	392	445	98
7	6	3	85	96	290
7	7	3	101	112	286
7	8	3	68	52	247
7	1	4	327	296	219
7	2	4	267	258	57
7	3	4	57	38	326
7	4	4	224	224	251
7	5	4	236	252	29
7	6	4	44	22	249
7	7	4	124	130	196
7	8	4	105	81	89
7	1	5	327	316	289
7	2	5	369	365	248
7	3	5	120	110	343
7	4	5	151	139	64
7	5	5	242	267	103
7	6	5	118	137	75
7	7	5	141	168	252
7	8	5	89	129	243
7	1	6	120	110	118
7	2	6	308	312	212
7	3	6	64	71	204
7	4	6	92	78	56
7	5	6	79	81	326
7	6	6	69	92	6
7	7	6	69	69	97
7	8	6	80	87	200
7	1	7	564	581	234
7	2	7	488	530	303
7	3	7	92	88	219
7	4	7	255	281	113
7	5	7	236	267	53
7	6	7	92	103	128
7	7	7	134	132	245
7	8	7	192–	186	297
7	1	8	389	386	107
7	2	8	212	201	209
7	3	8	42–	40	138
7	4	8	148	171	36
7	5	8	139	158	300
7	6	8	58	63	167
7	7	8	75	76	106
7	1	9	432	419	278
7	2	9	199	209	249
7	3	9	144	165	231
7	4	9	144	181	75
7	5	9	206	244	96
7	6	9	43	61	0
7	7	9	123	120	260
7	1	10	223	220	255
7	2	10	162	159	161
7	3	10	39–	20	356
7	4	10	132	146	345
7	5	10	136	135	77
7	6	10	73	76	228
7	7	10	57	52	249
7	1	11	182	184	355
7	2	11	380	393	248
7	3	11	48	31	283
7	4	11	261	313	52
7	5	11	160	188	172
7	6	11	44	55	59
7	1	12	68	70	266
7	2	12	170	154	150
7	3	12	85	11	110
7	4	12	103	103	284
7	5	12	48	29	98
7	6	12	57	68	7
7	1	13	236	246	248
7	2	13	232	249	299
7	3	13	67	77	224
7	4	13	127	138	79
7	5	13	118	133	90
7	1	14	228	238	165
7	2	14	93	80	321
7	3	14	39	37	129
7	4	14	79	76	151
7	5	14	135	160	341
7	1	15	292	314	258
7	2	15	61	58	242
7	3	15	39	43	229
7	4	15	74	83	74
7	5	15	80	82	158
7	6	16	43	33	78
7	3	16	13–	14	257
7	1	17	34	47	247
7	2	17	212	213	279
8	0	0	325	261	180
8	1	0	662	683	180
8	2	0	230	201	180
8	3	0	380	417	0
8	4	0	366	373	180
8	5	0	229	267	180
8	6	0	152	195	180
8	7	0	323	332	180
8	8	0	66	91	180
8	0	1	371	328	214
8	1	1	171	168	156
8	2	1	51	47	45
8	3	1	327	348	177
8	4	1	91	85	125
8	5	1	65	75	180
8	6	1	92	108	189
8	7	1	58	52	170
8	8	1	34	51	80
8	0	2	642	599	175
8	1	2	489	434	188
8	2	2	108	85	314
8	3	2	181	179	82
8	4	2	260	284	339
8	5	2	213	243	148
8	6	2	277	333	162
8	7	2	175	177	199
8	8	2	31	41	184
8	0	3	553	494	176
8	1	3	287	255	168
8	2	3	264	251	183
8	3	3	517	569	166
8	4	3	122	121	185
8	5	3	76	61	210
8	6	3	231	247	171
8	7	3	160	169	184
8	8	3	50	61	175
8	0	4	798	769	189
8	1	4	305	251	130
8	2	4	374	368	11
8	3	4	440	479	320
8	4	4	451	498	28
8	5	4	59	50	274
8	6	4	265	303	198
8	7	4	54	65	126
8	8	4	34	43	36
8	0	5	369	307	146
8	1	5	248	233	151
8	2	5	281	300	227
8	3	5	198	211	139
8	4	5	214	245	197
8	5	5	186	204	161
8	6	5	127	145	159
8	7	5	84	95	197
8	8	5	57–	57	222
8	0	6	93–	49	346
8	1	6	66–	11	281
8	2	6	348	344	352
8	3	6	596	667	9
8	4	6	219	236	309
8	5	6	81	95	316
8	6	6	33–	7	124
8	7	6	98	95	187
8	0	7	262	223	301
8	1	7	126	137	231
8	2	7	112	107	96
8	3	7	184	189	5
8	4	7	62	49	124
8	5	7	56	57	191
8	6	7	92	105	330
8	7	7	23–	32	300
8	0	8	222	203	133
8	1	8	306	294	291
8	2	8	314	304	338
8	3	8	291	316	28
8	4	8	380	433	348
8	5	8	39–	37	301
8	6	8	128	139	118
8	7	8	116	122	266
8	0	9	421	395	334
8	1	9	194	159	357
8	2	9	172	176	29
8	3	9	295	331	313
8	4	9	124	151	359

Table 3 (*cont.*)

h	k	l	$10F_o$	$10F_c$	α	h	k	l	$10F_o$	$10F_c$	α	h	k	l	$10F_o$	$10F_c$	α	h	k	l	$10F_o$	$10F_c$	α	h	k	l	$10F_o$	$10F_c$	α
8	5	9	115	123	0	9	5	3	241	256	94	9	1	15	218	225	274	10	2	8	164	157	174	11	3	5	33-	24	273	12	3	5	202	212	78
8	6	9	170	183	321	9	6	3	34-	12	342	9	2	15	87	85	221	10	3	8	133	150	85	11	4	5	29-	18	244	12	4	5	44	54	70
8	7	9	120-	108	0	9	7	3	109	115	288	10	0	0	146	137	0	10	4	8	64	75	145	11	5	5	91	81	59	12	5	5	126-	126	275
8	0	10	452	439	199	9	1	4	115	105	347	10	1	0	141	143	0	10	5	8	122	135	148	11	6	5	19-	24	145	12	0	6	130	114	140
8	1	10	175	164	143	9	2	4	219	190	13	10	2	0	339	330	0	10	6	8	73	151	155	11	1	6	154	130	72	12	1	6	118	103	59
8	2	10	94	90	26	9	3	4	76	79	55	10	3	0	302	302	0	10	0	9	609	619	280	11	2	6	337	356	357	12	2	6	88	69	41
8	3	10	383	430	324	9	4	4	166	183	166	10	4	0	187	231	0	10	1	9	110	101	296	11	3	6	39	41	327	12	3	6	116	118	137
8	4	10	181	208	41	9	5	4	91	91	227	10	5	0	117	115	0	10	2	9	106	102	81	11	4	6	183	223	163	12	4	6	56	70	34
8	5	10	32-	10	292	9	6	4	64	65	90	10	6	0	46	51	0	10	3	9	115	117	307	11	5	6	87	84	241	12	0	7	279	227	284
8	6	10	144	165	216	9	7	4	22-	28	32	10	7	0	42	34	180	10	4	9	115	132	78	11	1	7	129	115	284	12	1	7	145	131	259
8	0	11	301	302	333	9	1	5	270	241	328	10	0	1	352	332	205	10	5	9	34	32	322	11	2	7	92	80	233	12	2	7	91	86	177
8	1	11	198	171	336	9	2	5	298	285	259	10	1	1	184	168	46	10	0	10	132	97	142	11	3	7	28-	7	315	12	3	7	152	163	49
8	2	11	287	297	353	9	3	5	98	95	337	10	2	1	262	264	80	10	1	10	228	216	139	11	4	7	69	76	22	12	4	7	76	61	156
8	3	11	38	39	330	9	4	5	183	177	70	10	3	1	413	443	124	10	2	10	89	82	352	11	5	7	96	101	104	12	0	8	235	194	267
8	4	11	192	219	352	9	5	5	148	168	120	10	4	1	195	225	76	10	3	10	159	160	36	11	1	8	229	217	343	12	1	8	84	68	247
8	5	11	130	141	341	9	6	5	46	57	113	10	5	1	124	128	76	10	4	10	96	114	23	11	2	8	94	88	328	12	2	8	44	40	235
8	6	11	91	105	313	9	7	5	92	93	261	10	6	1	133	156	207	10	5	10	15-	26	103	11	3	8	58-	43	305	12	3	8	151	156	253
8	0	12	235	234	165	9	1	6	132	135	91	10	7	1	61	51	330	10	0	11	81	72	332	11	4	8	76	81	147	12	0	9	274	251	269
8	1	12	366	376	169	9	2	6	326	322	351	10	0	2	220	198	216	10	1	11	93	94	315	11	5	8	195-	196	178	12	1	9	109	92	265
8	2	12	63	73	115	9	3	6	45-	42	203	10	1	2	217	190	324	10	2	11	118	104	31	11	1	9	54-	25	155	12	2	9	69	77	113
8	3	12	243	262	354	9	4	6	181	208	161	10	2	2	130	116	330	10	3	11	151	153	61	11	2	9	159	155	264	12	3	9	13-	61	117
8	4	12	64	59	214	9	5	6	67	57	345	10	3	2	319	337	332	10	4	11	68	83	63	11	3	9	42	26	70	12	0	10	118	98	275
8	5	12	144	165	160	9	6	6	43	46	166	10	4	2	169	181	356	10	0	12	57	71	141	11	4	9	70	96	107	12	1	10	229	226	254
8	0	13	156	137	79	9	7	6	82	67	113	10	5	2	96	97	19	10	1	12	84	83	39	11	1	10	273	254	0	12	2	10	220-	196	245
8	1	13	79	79	313	9	1	7	399	362	220	10	6	2	68	68	244	10	2	12	168	169	353	11	2	10	49	47	40	12	0	11	133-	220	223
8	2	13	148	154	315	9	2	7	393	389	284	10	7	2	30	44	248	10	3	12	201	217	352	11	3	10	40	33	138	12	1	11	13-	56	329
8	3	13	89	86	126	9	3	7	127	117	259	10	0	3	486	393	228	10	4	12	110-	136	358	11	4	10	44	47	188	13	1	0	279	268	0
8	4	13	69	79	334	9	4	7	205	217	109	10	1	3	43	37	291	10	0	13	144	135	146	11	1	11	58	52	232	13	2	0	39	15	180
8	5	13	59	77	335	9	5	7	188	206	51	10	2	3	205	191	115	10	1	13	142	133	340	11	2	11	50	50	0	13	3	0	20-	17	0
8	0	14	509	508	159	9	6	7	120	125	126	10	3	3	196	201	146	10	2	13	192	205	43	11	3	11	34	40	74	13	4	0	15	27	0
8	1	14	153	145	202	9	7	7	11-	41	234	10	4	3	204	229	111	10	3	13	169	277	104	11	1	12	109	111	315	13	1	1	54	54	64
8	2	14	59	56	83	9	1	8	258	213	13	10	5	3	45	40	182	10	0	14	138	147	251	11	2	12	201-	205	24	13	2	1	55	57	114
8	3	14	105	119	123	9	2	8	62	50	192	10	6	3	145	161	217	10	1	14	87	92	357	12	0	0	109-	8	180	13	3	1	38	28	71
8	4	14	74	79	21	9	3	8	43-	34	310	10	7	3	14-	10	124	11	1	0	327	338	0	12	1	0	132	122	0	13	4	1	69	74	295
8	0	15	115	106	135	9	4	8	75	83	7	10	0	4	537	505	199	11	2	0	211	215	0	12	2	0	61	62	180	13	1	2	98	99	355
8	1	15	132	122	179	9	5	8	184	210	170	10	1	4	222	209	170	11	3	0	67	63	180	12	3	0	110	118	180	13	2	2	165	154	356
8	2	15	91	94	181	9	6	8	24-	34	249	10	2	4	153	136	284	11	4	0	42	45	180	12	4	0	26-	5	180	13	3	2	19-	21	134
8	3	15	120	141	95	9	1	9	338	311	266	10	3	4	229	239	331	11	5	0	128	142	180	12	5	0	82	84	0	13	4	2	79	91	191
8	0	16	257	276	194	9	2	9	142	148	249	10	4	4	111	116	322	11	6	0	18-	24	180	12	0	1	199	189	256	13	1	3	141	127	99
8	1	16	124	132	150	9	3	9	39-	7	23	10	5	4	105	103	185	11	1	1	171	176	290	12	1	1	69	73	313	13	2	3	51	40	27
8	2	16	38	46	60	9	4	9	178	206	107	10	6	4	163	183	210	11	2	1	96	99	214	12	2	1	228	228	78	13	3	3	34	31	3
9	1	0	193	151	0	9	5	9	176	189	77	10	7	4	98-	80	183	11	3	1	37-	41	239	12	3	1	79	86	104	13	4	3	13	38	221
9	2	0	116	100	0	9	6	9	33	49	308	10	0	5	139	89	299	11	4	1	65	85	43	12	4	1	193	217	96	13	1	4	96	74	283
9	3	0	58	48	0	9	1	10	225	223	8	10	1	5	443	438	239	11	5	1	75	79	135	12	5	1	21-	38	55	13	2	4	249	239	24
9	4	0	124	121	180	9	2	10	97	113	256	10	2	5	236	220	210	11	6	1	48	48	41	12	0	2	204	182	74	13	3	4	16-	26	350
9	5	0	44	26	0	9	3	10	75	62	97	10	3	5	278	296	76	11	1	2	260	271	335	12	1	2	241	231	99	13	1	5	88	71	141
9	6	0	109	121	180	9	4	10	56	52	28	10	4	5	103	106	203	11	2	2	204	196	42	12	2	2	198	191	84	13	2	5	92	89	70
9	7	0	72	64	0	9	5	10	163	174	193	10	5	5	192	210	248	11	3	2	78	85	304	12	3	2	114	114	52	13	3	5	14-	29	90
9	1	1	335	313	267	9	6	10	11-	15	211	10	6	5	75	82	304	11	4	2	122	135	252	12	4	2	178	212	94	13	1	6	51	135	19
9	2	1	491	484	288	9	1	11	152	144	343	10	0	6	349	305	172	11	5	2	220	256	150	12	5	2	104	138	101	13	2	6	102	104	313
9	3	1	115	121	194	9	2	11	238	229	261	10	1	6	313	293	190	11	6	2	25	30	175	12	0	3	187	163	259	13	3	6	11-	38	29
9	4	1	287	296	111	9	3	11	70	56	3	10	2	6	132	134	140	11	1	3	75-	64	33	12	1	3	152	138	282	13	1	7	70	63	4
9	5	1	128	143	78	9	4	11	121	129	81	10	3	6	42	31	175	11	2	3	80	73	276	12	2	3	127	116	39	13	2	7	21-	87	98
9	6	1	104	107	92	9	5	11	79	92	138	10	4	6	104	106	200	11	3	3	35-	30	231	12	3	3	237	245	104	13	1	8	24-	144	43
9	7	1	111	104	304	9	1	12	92	77	248	10	5	6	172	190	198	11	4	3	81	95	90	12	4	3	67	78	49	14	0	0	327	284	0
9	1	2	416	371	305	9	2	12	231	235	13	10	6	6	165	193	177	11	5	3	65	60	240	12	5	3	18-	26	290	14	1	0	117	110	0
9	2	2	281	258	84	9	3	12	29-	17	149	10	0	7	255	233	263	11	6	3	45	43	21	12	0	4	385	356	72	14	0	1	344	310	275
9	3	2	108	103	345	9	4	12	171	189	220	10	1	7	306	296	265	11	1	4	100	103	2	12	1	4	169	143	91	14	1	1	135	124	248
9	4	2	166	175	242	9	5	12	87-	73	86	10	2	7	118	112	278	11	2	4	242	256	343	12	2	4	197	207	37	14	0	2	190	178	11
9	5	2	214	243	126	9	1	13	192	194	249	10	3	7	72	70	137	11	3	4	45	46	62	12	3	4	246	254	79	14	1	2	120	116	353
9	6	2	35-	31	180	9	2	13	142	143	287	10	4	7	70	83	274	11	4	4	170	204	165	12	4	4	126	134	90	14	0	3	106	93	164
9	7	2	157	158	312	9	3	13	27	32	281	10	5	7	153	174	238	11	5	4	104	126	107	12	5	4	66	86	88	14	1	3	142	139	285
9	1	3	416	370	282	9	4	13	56	60	86	10	6	7	140	162	271	11	6	4	13-	8	20	12	0	5	157	109	280	14	0	4	39	71	332
9	2	3	183	167	167	9	1	14	64	63	277	10	0	8	277	244	169	11	1	5	82	85	216	12	1	5	222	207	267	14	1	4	21-	26	55
9	3	3	92	86	242	9	2	14	99	104	17	10	1	8	198	196	164	11	2	5	64	61	1	12	2	5	45-	22	179	14	0	5	22-	46	167

At the end of the refinement the atomic parameters were as reported in Table 1, which also gives the e.s.d.'s (Cruickshank, 1949, 1950) and the ratios $|r| = (\text{e.s.d.})/(\text{shift})$ for each coordinate. The B_{ij}'s were determined by the method of Nardelli & Fava (1960) using the second derivatives of the electron density in the differential synthesis; their e.s.d.'s were calculated following Cruickshank (1956). In Table 2 the observed atomic peak shapes are compared with the calculated ones. The structure factors reported in Table 3 are calculated with the final parameters of Table 1 using the atomic scattering factors of Thomas & Umeda (1957) for Zn^{2+}, of Dawson (1960) for S and of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for O, N and C.

No attempt was made to locate the hydrogen atoms directly. Their coordinates, reported in Table 4, were calculated assuming an sp^2 bond configuration for each nitrogen atom with a distance N–H of 1·03 Å: with these coordinates unacceptable contacts are not observed. In Table 4, the values of the electron density found at the points corresponding to the assumed coordinates of the hydrogen atoms are also reported.

Table 4. *Calculated fractional coordinates* ($\times 10^3$) *and corresponding values of* ϱ_0 *for hydrogen atoms in thiourea molecules*

	x/a	*y/b*	*z/c*	ϱ_o
H(1)	256	−499	−237	0·6 e.Å^{-3}
H(2)	117	−199	−275	0·6
H(3)	−41	−100	−83	1·1
H(4)	−52	−192	−188	1·0
H(5)	−33	−345	220	0·6
H(6)	−159	−212	196	1·2
H(7)	141	−308	145	0·7
H(8)	152	−147	64	0·9
H(9)	−291	573	−92	1·1
H(10)	−206	490	−180	0·8
H(11)	−86	403	64	1·3
H(12)	−222	523	49	0·8

All the calculations were performed on the Olivetti Elea 6001/S computer of the Centro di Calcolo Elet-

tronico of the University of Parma, using the programs of Nardelli, Musatti, Domiano & Andreetti (1964, 1965).

Discussion

Fig. 1 represents a clinographic projection of a coordination polyhedron, showing that each zinc atom is tetrahedrally surrounded by three sulphur atoms from three thiourea molecules and one oxygen atom from a sulphate group. Distances and angles in the coordination polyhedron are:

Zn–S(2)	2·332 ± 4 Å
Zn–S(3)	2·309 ± 4
Zn–S(4)	2·323 ± 4
Zn–O(1)	1·975 ± 9
S(2)–Zn–S(3)	114·6 ± 0·1°
S(2)–Zn–S(4)	102·4 ± 0·1
S(3)–Zn–S(4)	111·1 ± 0·1
S(2)–Zn–O(1)	107·4 ± 0·3
S(3)–Zn–O(1)	113·9 ± 0·3
S(4)–Zn–O(1)	106·6 ± 0·3

Little significance can be attributed to the differences among the three Zn–S bond distances, which are comparable to the sum of Pauling's covalent radii (2·35 Å) and to the values found in other tetrahedral zinc compounds [*e.g.* 2·261 ± 0·004, 2·326 ± 0·002 Å in bis(thiourea)zinc acetate (Cavalca, Fava Gasparri, Andreetti & Domiano, 1966), 2·331 ± 0·003, 2·355 ± 0·003 and 2·383 ± 0·002 Å in bis(diethyldithiocarbamate)zinc (Bonamico, Mazzone, Vaciago & Zambonelli, 1965), 2·286 ± 0·006 and 2·298 ± 0·006 Å in mono(thiosemicarbazide)zinc chloride (Cavalca, Nardelli & Branchi, 1960) and 2·35 ± 0·01 Å in bis(thiourea)zinc chloride (Kunchur & Truter, 1958)].

The Zn–O (1·975 ± 0·009 Å) distance agrees with the values usually found in tetrahedral zinc complexes [*e.g.* 1·973 ± 0·006 and 1·954 ± 0·008 Å in bis(thiourea)zinc acetate].

The orientation of the SO_4^{2-} group is determined by the Zn–O(1) interaction (Zn–O(1)–S(1)125·6 ± 0·6°) and by the hydrogen bonding involving the oxygen atoms and the NH_2 groups. These effects are also responsible for the lack of C_{3v} symmetry in the coordination polyhedron. The distances and angles in the SO_4^{2-}

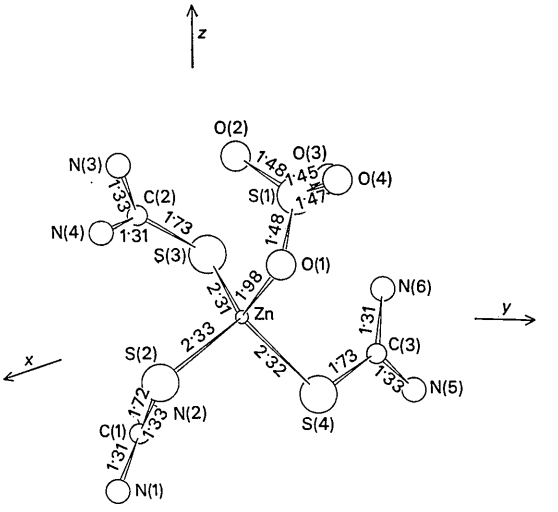

Fig. 1. Clinographic projection of a coordination polyhedron

Table 5. *Bond lengths and angles in some sulphates*

	S–O Range	S–O σ_{max}	Angle O–S–O Range	Angle O–S–O σ_{max}	
Present work	1·454–1·480 Å	0·014 Å	107·5–110·6°	0·7°	
Cd*tu*$SO_4.2H_2O$	1·44—1·48	0·020	108·0–111·3	1·1	Cavalca, Domiano, Fava Gasparri & Boldrini (1967).
$Li_2SO_4.H_2O$	1·473–1·487	0·002	108·4–110·9	0·1	Larson (1965).
$(CH_3NH)[Al(H_2O)_6](SO_4)_2.6H_2O$	1·473–1·494	0·005	109·2–109·6	0·3	Okaya, Ahmed, Pepinsky & Vand (1957).
$ZrSO_4.4H_2O$	1·443–1·486	0·020	106·9–112·5	0·8	Singer & Cromer (1959).
$Mg(NH_4)_2(SO_4)_2.6H_2O$	1·459–1·481	0·005	108·4–110·7	0·3	Margulis & Templeton (1962).
$Ni(NH_4)_2(SO_4)_2.6H_2O$	1·470–1·486	0·015	108·6–110·5	0·6	Montgomery & Lingafelter (1964*b*).
$MgSO_4.4H_2O$	1·466–1·480	0·006	— —	—	Baur (1964*a*).
$MgSO_4.6H_2O$	1·460–1·482	0·003	— —	—	Zalkin, Ruben & Templeton (1964).
$MgSO_4.7H_2O$	1·460–1·482	0·004	108·6–110·2	0·3	Baur (1964*c*).
$[CH_3SC(NH_2)_2]_2SO_4$	1·456–1·470	0·006	109·0–109·8	0·4	Stam (1962).
$Zn(NH_4)_2SO_4.6H_2O$	1·462–1·488	0·015	108·3–110·5	0·6	Montgomery & Lingafelter (1964*a*).
$CoSO_4.6H_2O$	1·45—1·51	0·030	— —	—	Zalkin, Ruben & Templeton (1962).
$Ni(NH_4)_2(SO_4)_2$	1·46—1·52	0·025	109·3–109·7	4·0	Grimes, Kay & Webb (1963).
$Li(N_2H_5).SO_4$	1·45—1·50	0·030	108·2–110·2	1·0	Brown (1964).
$HgSO_4.H_2O$	1·46—1·49	0·020	109·0–110·0	1·0	Templeton, Templeton & Zalkin (1964).
$FeSO_4.7H_2O$	1·462–1·488	0·004	108·4–110·1	0·3	Baur (1964*b*).
$(NH_4)_2Cu(SO_4)_2.6H_2O$	1·466–1·484	0·005	108·6–110·6	0·2	Montgomery & Lingafelter (1966*a*).
$(NH_3)_5CoO_2Co(NH_3)_5.SO_4(HSO_4)_3$	1·421–1·483	0·020	106·3–114·3	2·0	Schaefer & Marsh (1966).
$CsAl(SO_4)_2.12H_2O$	1·473–1·479	0·009	109·0–109·9	2·0	Cromer, Kay & Larson (1966).
$NaNH_4SO_4.2H_2O$	1·452–1·492	0·014	107·8–110·9	0·7	Corazza, Sabelli & Giuseppetti (1967).
$Cd(NH_4)_2(SO_4)_2.6H_2O$	1·459–1·483	0·008	108·0–111·4	0·3	Montgomery & Lingafelter (1966*b*).
$Mn(NH_4)_2(SO_4)_2.6H_2O$	1·452–1·475	0·007	108·5–110·1	0·3	Montgomery & Lingafelter (1966*c*).
$Cu_2(NH_2CH_3)_4(OH)_2SO_4.H_2O$	1·464–1·495	0·016	108·0–111·7	1·1	Iitaka, Shimizu & Kwan (1966).
$CuSO_4.5H_2O$	1·467–1·490	—	— —	—	Bacon (1962).

group are in good agreement with those generally observed in some sulphates, as quoted in Table 5:

S(1)–O(1)	1·474 ± 10 Å
S(1)–O(2)	1·480 ± 13
S(1)–O(3)	1·454 ± 14
S(1)–O(4)	1·474 ± 12
O(1)–S(1)–O(2)	109·4 ± 0·6°
O(1)–S(1)–O(3)	110·1 ± 0·6
O(1)–S(1)–O(4)	107·5 ± 0·6
O(2)–S(1)–O(3)	110·6 ± 0·7
O(2)–S(1)–O(4)	108·8 ± 0·7
O(3)–S(1)–O(4)	110·3 ± 0·7

The three independent thiourea molecules are planar: their least-squares planes are quoted in Table 6 with bond distances and angles. From these values, if compared with those found in uncomplexed thiourea, it is clear that coordination does not significantly influence the dimensions of the ligand as observed for bis-(thiourea)zinc acetate. The three thiourea molecules are tilted with respect to the Zn–S bonds by the angles Zn–S(2)–C(1) 101·9 ± 0·4°, Zn–S(3)–C(2) 107·7 ± 0·4° and Zn–S(4)–C(3) 107·0 ± 0·5°, which are consistent with those found in other thiourea complexes [*e.g.* 100·6 ± 0·3° and 101·2 ± 0·3° in bis(thiourea)zinc acetate; 113° in bis(thiourea)cadmium chloride (Nardelli, Cavalca & Braibanti, 1957), 108·6° in bis(thiourea)zinc chloride (Kunchur & Truter, 1958), 105°, 108°, 113° in tris(thiourea)copper(I) chloride (Okaya & Knobler, 1964)].

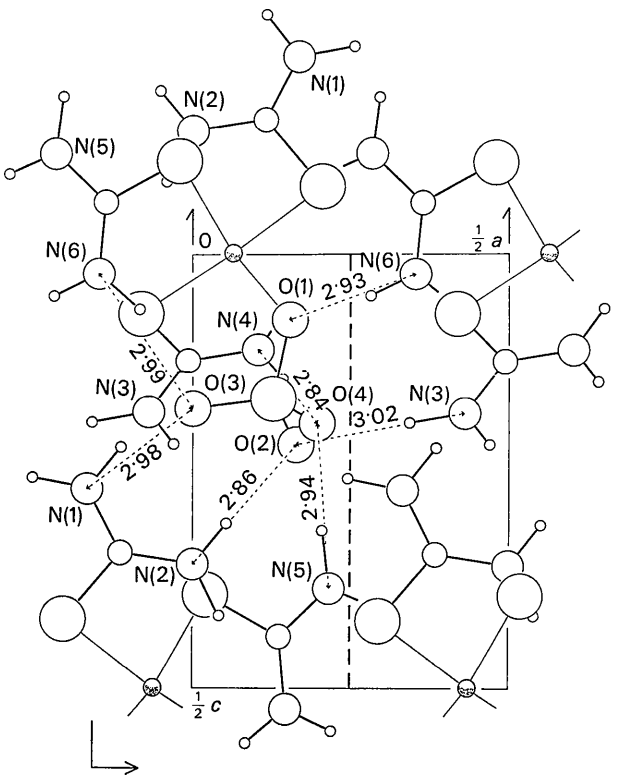

Fig. 2. $Znt u_3(SO_4)$. Diagrammatic projection of the structure along [010].

The following N···O distances can be considered as hydrogen bonds (the corresponding H–N–O angles are quoted in square brackets; the e.s.d.'s are all 0·01 Å):

N(6^{iv})–H(12^{iv})	... O(1)	2·93 Å	[8·4°]
N(2^{i}) –H(4^{i})	... O(2)	2·86	[17·5]
N(3^{ii}) –H(6^{ii})	... O(2)	3·02	[7·5]
N(6) –H(11)	... O(3)	2·99	[1·6]
N(1^{i}) –H(2^{i})	... O(3)	2·98	[17·5]
N(5^{iii})–H(10^{iii})	... O(4)	2·94	[8·1]
N(4^{v}) –H(7^{v})	... O(4)	2·84	[8·9]

The packing in the crystal and the orientation of the thiourea molecules are determined by these interactions [Fig. 2]. Other distances less than 3·5 Å are as follows:

S(1)–N(3^{ii})	3·46 Å
S(2)–S(3^{ii})	3·30
S(3)–N(1^{i})	3·47
O(2)–N(1^{vi})	3·31
O(3)–N(3^{v})	3·02
O(3)–N(2^{i})	3·37
O(4)–N(1^{vii})	3·43
O(4)–N(3^{ii})	3·23
O(4)–N(6^{iv})	3·18
N(3)–N(1^{i})	3·46

The superscripts have the following significance:

i	$\bar{x},\bar{y},z+\frac{1}{2}$	v	$x,1+y,z$
ii	$x+\frac{1}{2},\bar{y},z$	vi	$\frac{1}{2}-x,y,z+\frac{1}{2}$
iii	$x,1-y,z+\frac{1}{2}$	vii	$\frac{1}{2}-x,1+y,z+\frac{1}{2}$
iv	$x+\frac{1}{2},1-y,z$	viii	$\bar{x}-\frac{1}{2},1-y,z$

This work was done with the financial support of the Consiglio Nazionale delle Ricerche (Roma).

Table 6. *Least-squares planes, bond distances and angles for the thiourea molecules*

tu(1)	S(2)C(1)N(1)N(2)	$-0·2415x+0·8960y-0·3727z=-0·1095$
tu(2)	S(3)C(2)N(3)N(4)	$0·3083x+0·6625y+0·6827z=0·4364$
tu(3)	S(4)C(3)N(5)N(6)	$-0·5300x-0·8473y+0·0349z=-2·1095$

	S–C	C–N	S–C–N	N–C–N
tu(1)	1·717 ± 13	1·310 ± 17–1·330 ± 18	116·7 ± 1·1–125·5 ± 0·9°	120·7 ± 1·3°
tu(2)	1·731 ± 14	1·326 ± 18–1·305 ± 20	117·0 ± 1·1–123·7 ± 1·1	119·3 ± 1·4
tu(3)	1·725 ± 17	1·327 ± 16–1·308 ± 19	115·8 ± 0·9–123·4 ± 1·1	120·8 ± 1·1
*tu**	1·720 ± 9	1·340 ± 6	120·5 ± 0·5	119·0 ± 0·5

* Uncomplexed (Truter, 1967).

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Ein Beitrag zur Kristallchemie der Schichtsilikate

VON F. LIEBAU

Mineralogisch-Petrographisches Institut der Universität Kiel, Deutschland

(*Eingegangen am* 3. *April* 1967)

Herrn Prof. Dr. G. Menzer zum 70. *Geburtstag gewidmet*

The great number of $[Si_2O_5]$-layer silicates is primarily due to the differences in size and charge of the cations. Anhydrous layer-silicates show an increasing degree of convolution of layers with decreasing radius/charge ratio of cations, the size of cation sites between layers decreasing at the same time. This explains why 1+ cations form anhydrous layer silicates and 2+ cations of small or medium size and 3+ cations do not. In hydrous layer silicates the $[MeO(OH)_n]$ polyhedra are 'effective' cations. The deviation froma plane conformation increases with increasing ratio radius/charge, from $Al_4[Si_4O_{10}](OH)_8$ and the bent serpentines to the ruffled ones of pyrosmalite and apophyllite.

Zu der grossen Gruppe der Schicht- oder Phyllosilikate zählen bekanntlich alle die Silikate, bei denen die $[SiO_4]$-Tetraeder über gemeinsame Sauerstoffatome zu zweidimensional ausgedehnten Schichten verknüpft sind. Wenn auch die Art der Verknüpfung der Tetraeder zu Schichten und damit deren Symmetrie sehr verschieden sein kann – eine systematische Übersicht gibt Liebau (1962) – so gleichen sich doch alle bisher beschriebenen Silikatschichten darin, dass jedes ihrer $[SiO_4]$-Tetraeder über gemeinsame Sauerstoffatome an