Inorganica Chimica Acta, 23 (1977) 117–129

The Crystal Structure of K$_3$Cu(NO$_2$)$_3$

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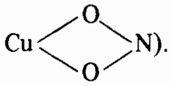
Received October 14, 1976

The compound crystallizes in the orthorhombic system, space group D_{2h}^{16}-Pbnm with cell constants of a = 21.70(4), b = 18.94(4) and c = 10.88(2) Å. The unit cell volume, observed and calculated densities are, respectively, 4471.66 Å^3, 2.46(2) g cm^{-3} and 2.44 g cm^{-3}. There are 16 molecules of K$_3$Cu(NO$_2$)$_5$ in the unit cell and the anions crystallize in the lattice as four *independent Cu(NO$_2$)$_5^{3-}$ species located at positions (c) of the space group. Molecularly, they are identical in pairs inspite of being crystallographically independent from one another. One Cu(NO$_2$)$_5^{3-}$ species is bound through the nitrogen of three NO$_2^-$ ligands and by two in a symmetrical, bidentate fashion (*i.e.,



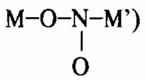
).

The other type of Cu(NO$_2$)$_5^{3-}$ species present in the lattice contains all modes of coordination of NO$_2^-$ when bound to a single metal center. That is, there are two monodentate Cu–NO$_2$ bonds, two monodentate Cu–O–N–O bonds and one symmetrical, bidentate attachement of the type described above. There are eight crystallographically independent potassium ions in the lattice: four sit at general positions while the other four are found at mirror planes. The coordination around the potassium ions is irregular and determined primarily by packing considerations dictated by the anions. The coordination number of the potassiums vary considerably and the exact number of ligands around each depends on the length of the radius one is willing to consider reasonable for bonding. Details are discussed in the text.

Introduction

The shape of the coordination sphere around a metal ion (M) in a complex with composition MX$_5$ or AMX$_5$ (where A = a charge compensating cation(s) and X = any potential monodentate ligand such as Cl$^-$, SCN$^-$, NO$_2^-$, *etc.*) has been the object of considerable speculation and research. Two recent reviews [5, 6] summarize the results obtained up to 1972 and it is clear from these reports that chemical composition is a poor guide for the prediction of pentacoordination in such compounds. For example, Cu(NO$_3$)$_2$ [7], Cu(NO$_3$)$_2$(O$_2$N–CH$_3$) [8a] and Cu(O$_2$N–CH$_3$) [8b] contain pentacoordinated Cu(II) ions. On the other hand, the compound with composition (NH$_4$)[Cu(NH$_3$)$_5$](ClO$_4$)$_3$ has been found to contain planar Cu(NH$_3$)$_4^{2+}$ cations [9] and the compound originally formulated as K$_3$Hg(NO$_2$)$_5$ has been found [10, 11] to contain one simple NO$_3^-$ lattice ion and an eight-coordinated (however, see ref. 11b) Hg(NO$_2$)$_4^{2-}$ anion. Finally, there are large numbers of compounds in which the central cation achieves higher coordination numbers through polymerization; a simple of example of these being Tl$_2$AlF$_5$ [12] in which the aluminium is six-coordinate and there are many other examples discussed in detail in standard references [13].

The NO$_2^-$ anion can bind a metal through its nitrogen [14], through one of its oxygens [15, 16] and it can act as a bidentate ligand to a single metal ion [11, 17]. It can also act as a bidentate bridge to two metal centers and in that case the bridge can either be symmetrical (*i.e.*, M–O–N–O–M') or it can be asymmetric (*i.e.*,



$$\text{M–O–}\underset{\substack{|\\ \text{O}}}{\text{N}}\text{–M'})$$

[18, 19]. Therefore, given the variety of coordination shapes and modes of ligand binding that could, in theory, occur with a compound having composition K$_3$Cu(NO$_2$)$_5$, we decided to determine its crystal structure. The unexpected results are given below. In an earlier report [20] one of us (I. B.) had discussed the magnetic and spectral properties of this substance.

Experimental

The compound was made according to the procedure of Kurtenacker [21] and its characterization by elemental analysis and other physical measurements has already been given in detail elsewhere [20]. Crystals of K$_3$Cu(NO$_2$)$_5$ were obtained from material which had been recrystallized five times from methanol and then redissolved in methanol and kept at 0 °C for many days till crystals slowly deposited at the bottom of the beaker. This procedure was found necessary to obtain suitable specimens for single crystal X-ray diffraction. The resulting green–black needles were cleaved to suitable size by slicing them in the direction perpendicular to the needle axis and the specimen used for data collection was 0.2 × 0.3 × 0.4 mm and was bound by the (110), ($\bar{1}\bar{1}0$), ($\bar{1}10$), ($1\bar{1}0$), (001) and ($00\bar{1}$) faces. Other crystallographic data of importance are: M. W. = 410.87 g mol^{-1}; a = 21.70(4), b = 18.94(4) and c = 10.88(2) Å; V = 4471.66 Å^3/unit cell, d_o = 2.46(2) g cm^{-3} (flotation in bromoform/bromobenzene) and F(000) = 2896 electrons. The density calculated for z = 16 molecules/unit cell is 2.44 g cm^{-3}, in good agreement with the observed value. Examination of films recorded in precession and Weissenberg cameras gave the following systematic extinctions: Okl with $k \neq 2n$ and h0l with $h + l \neq 2n$, which imply that the space group is either D_{2h}^{16}-Pbnm or C_{2v}^{9}-Pbn2$_1$. The former choice leads to the result that for the asymmetric unit four coppers, four potassiums, twelve oxygens and twelve nitrogen atoms occupy the four-fold set of positions (c) in the space group Pbnm while the other 22 atoms in the asymmetric unit occupy the general eight-fold set. The choice of the acentric space group Pbn2$_1$ removes the necessity of placing atoms in special positions but requires that 228 positional parameters be specified, instead of the 130 required for the centrosymmetric choice. We decided to proceed at the beginning on the assumption that the centrosymmetric choice was the correct one, as suggested by a Wilson [22] plot and by a negative piezoelectric test.

The data crystal was mounted in a thin-walled capillary tube since the substance is sensitive to moisture and experience with film studies showed that X-ray seem to enhance this sensitivity, while X-ray by themselves (glass encased samples) do not seem to have any effect on crystal stability. Data were collected with a General Electric XRD-6 Goniostant using the θ–2θ scan technique and Mo Kα radiation (λ = 0.71069 Å). Approximately 2500 reflections were sampled in the hkl octant to a 2θ = 41°. Of these, 1225 had satisfactory peak-to-background ratio and were, thus recorded. The resulting intensities were corrected for Lorentz and polarization effects and for absorption (μ = 3.18 cm^{-1} for Mo Kα radiation [23a]).

Solution and Refinement of the Structure

An absolute scale factor and a mean isotropic temperature factor were obtained by means of Wilson statistics [22]. A three dimensional sharpened, origin-removed Patterson function was then computed from the corrected intensities and which proved difficult to interpret unambiguously for the copper and potassium atom positions since it appeared that some atoms were in special positions but it was not clear which set of special positions were involved. Several trial sets were used which gave relatively high R-factors (*ca.* 70% on F^2) and which did not differ significantly from one another. Thus, we decided to abandon this approach and try direct methods. The programs used for the calculation of normalized structure factors and for the direct methods have been described in detail elsewhere [24]. Three reflections were assigned a positive phase, thereby fixing the origin for the space group Pbnm. Several reflections were assigned a phase on the basis of the Σ_1 relation and three symbolic phases, a, b and c were assigned. These data are summarized in Table I.

TABLE I. Reflections Phases.

h	k	l	E	Phase
Reflections whose Phases were Assigned by the Σ_1 Relation				
0	8	4	3.3333	+
0	8	8	3.7599	+
8	0	4	3.1320	+
8	8	0	3.4557	+
8	8	8	2.6807	+
16	0	0	3.4025	+
Origin Defining Reflections				
2	10	5	4.2584	+
14	3	4	2.2942	+
15	2	4	2.1477	+
Reflections to which Symbols a, b and c were Assigned and Eventual Sign Assigned to such Symbols				
4	4	4	4.6386	– = a
2	6	8	3.3000	+ = b
18	5	4	1.7727	+ = c

Eventual assignment of signs to the symbols a, b and c gave phases for 297 of the 410 reflections for which |E|>1.0. An E map calculated using the sign assignments for a, b and c (Table I) gave positions for the potassium and copper atoms and a difference Fourier, based on the phases determined by these atoms, gave light atoms which made chemical sense. Eventual refinement of the structure (*vide infra*) indicates that the choice of space group and the signs assigned to the symbolic phases (a, b and c) are probably the correct ones. No attempt was made to use the acentric choice of space group. The scattering curves used were those of Cromer [23d], which were modified by the effects of anomalous dispersion for the copper and potassium atom [23b]. Refinement of the positional and anisotropic thermal parameters for the four copper and eight potassium ions in the asymmetric unit plus the positional and isotropic thermal parameters of the light atoms gave residuals

$$R_1(F) = \Sigma|(|F_o| - |F_c|)|/\Sigma|F_o| = 0.056$$

TABLE II. Positional Parameters Multiplied by 10^4. Anisotropic Thermal Parameters Multiplied by 10^5 and Isotropic Thermal Parameters Multiplied by 10.

	x	y	z	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	2517(1)	1267(1)	2500(–)	76(6)	121(9)	339(34)	– 4(5)	–	–
Cu(2)	0062(1)	3685(1)	2500(–)	81(6)	154(10)	268(33)	3(6)	–	–
Cu(3)	4984(1)	3736(1)	2500(–)	– 86(6)	143(10)	381(34)	6(6)	–	–
Cu(4)	2658(1)	3868(1)	–2500(–)	– 57(6)	130(8)	428(31)	13(6)	–	–
K(1)	0079(2)	3432(3)	–2500(–)	–133(13)	206(19)	276(54)	– 6(12)	–	–
K(2)	0101(2)	1674(3)	2500(–)	–109(13)	179(17)	446(59)	– 2(11)	–	–
K(3)	2510(2)	4150(3)	2500(–)	–122(14)	215(18)	455(61)	– 7(12)	–	–
K(4)	2528(2)	0913(3)	–2500(–)	– 95(13)	161(17)	466(58)	– 2(11)	–	–
K(5)	3665(2)	2515(2)	0099(3)	–113(8)	207(11)	549(46)	–17(7)	10(17)	8(19)
K(6)	1545(2)	2642(2)	–0123(3)	–118(9)	230(11)	651(45)	21(8)	21(16)	–19(18)
K(7)	1052(2)	0078(2)	–0086(3)	–116(9)	259(12)	416(41)	32(8)	– 2(15)	41(19)
K(8)	3945(2)	0061(2)	0014(3)	– 87(8)	212(11)	877(50)	2(8)	4(15)	–94(21)
O(1)	2028(4)	1242(5)	0032(9)	– 29(2)					
O(2)	3006(4)	1149(5)	0035(9)	– 29(2)					
O(3)	2583(4)	2723(5)	1533(10)	– 29(2)					
O(4)	4574(5)	1401(5)	–0040(10)	– 27(2)					
O(5)	0557(4)	3604(5)	0031(10)	– 29(2)					
O(6)	0030(5)	4907(6)	–1519(11)	– 31(2)					
O(7)	4867(5)	2920(6)	1158(12)	43(3)					
O(8)	0414(6)	1436(7)	–0020(13)	57(3)					
O(9)	0014(6)	–0118(8)	1572(2)	60(4)					
O(10)	3769(4)	3863(5)	1523(10)	33(2)					
O(11)	2146(5)	4085(6)	–0013(9)	37(2)					
O(12)	2788(4)	4635(5)	–1113(10)	31(2)					
O(13)	2623(5)	2776(6)	–1551(12)	48(3)					
O(14)	3871(4)	3710(5)	–1517(10)	29(2)					
O(15)	3726(7)	1604(9)	2500(–)	41(4)					
O(16)	3357(9)	0582(11)	2500(–)	63(5)					
O(17)	1402(10)	1345(11)	2500(–)	65(5)					
O(18)	1805(9)	0403(11)	2500(–)	64(5)					
O(19)	1174(8)	3922(10)	2500(–)	58(4)					
O(20)	0829(8)	2909(9)	2500(–)	47(4)					
O(21)	3846(7)	1181(9)	–2500(–)	49(4)					
O(22)	4340(8)	2124(8)	–2500(–)	44(4)					
O(23)	1225(7)	0771(8)	–2500(–)	33(3)					
O(24)	1169(7)	1885(9)	–2500(–)	44(4)					
O(25)	1397(7)	3481(8)	–2500(–)	36(3)					
O(26)	1521(6)	4594(8)	–2500(–)	32(3)					
N(1)	2517(4)	1211(6)	0637(12)	20(3)					
N(2)	0071(5)	3622(6)	0660(11)	17(2)					
N(3)	0074(6)	1961(7)	–0136(15)	36(3)					
N(4)	2534(5)	4559(7)	–0076(14)	33(3)					
N(5)	1349(11)	0730(12)	2500(–)	50(5)					
N(6)	2548(7)	2370(8)	2500(–)	16(4)					
N(7)	3768(12)	0947(14)	2500(–)	68(6)					
N(8)	3865(11)	1815(13)	–2500(–)	55(6)					
N(9)	–0003(8)	4775(10)	2500(–)	37(5)					
N(10)	1282(9)	3293(10)	2500(–)	33(4)					
N(11)	0905(8)	1293(9)	–2500(–)	26(4)					
N(12)	4977(11)	5161(14)	2500(–)	63(7)					
N(13)	4058(7)	3828(9)	2500(–)	23(4)					
N(14)	1752(8)	3988(9)	–2500(–)	25(4)					
N(15)	2583(8)	2439(11)	–2500(–)	33(4)					
N(16)	3570(7)	3767(8)	–2500(–)	21(3)					

$R_2(F) = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2} = 0.075$ with an error of fit $= [\Sigma w(F_o - F_c)^2/(NO - NV)]^{1/2} = 1.59$.

where NO and NV are the number of observations and variables, respectively and w, the weights were calculated from the expressions $w = 4F_o^2/\sigma^2(F_o^2)$ and

TABLE III. Bond Lengths in Å.

Cu 1–N 1	2.03(1)	Cu 3–N 11	2.02(2)
–N 6	2.09(2)	–N 13	2.02(2)
–O 16	2.24(2)	–O 7	2.14(1)
–O 18	2.25(2)	–O 9	2.39(2)
–O 17	2.42(2)	...N 12[a]	2.70(3)
–O 15	2.70(2)	...O 24[a]	2.83(2)
...N 5[a]	2.73(2)	...O 10[a]	2.85(1)
...N 7	2.78(3)		
Cu 2–N 2	2.01(1)	Cu 4–N 14	1.98(2)
–N 9	2.07(2)	–N 16	1.99(2)
–O 22	2.19(2)	–O 12	2.11(1)
–O 20	2.22(2)	–O 13	2.31(1)
–O 19	2.45(2)	...N 15	2.71(2)
–O 21	2.65(2)	...O 26	2.82(2)
...N 8[a]	2.76(2)	...O 14	2.86(1)
...N 10	2.75(2)		
N 4–O 11	1.23(1)	N 10–O 19	1.21(2)
–O 12	1.26(2)	–O 20	1.22(2)
N 5–O 17	1.17(2)	N 11–O 23	1.21(2)
–O 18	1.17(2)	–O 24	1.26(2)
N 6–O 3	1.25(1)	N 12–O 9	1.14(2)
N 7–O 16	1.13(3)	N 13–O 10	1.24(1)
–O 15	1.25(3)	N 14–O 25	1.23(2)
N 8–O 22	1.19(3)	–O 26	1.25(2)
–O 21	1.20(3)	N 15–O 13	1.22(1)
N 9–O 6	1.23(1)	N 16–O 14	1.26(1)
K 1–O 25	2.86(2)	K 4–O 23	2.84(2)
–O 15	2.94(2)	–O 21	2.91(2)
–O 5	2.96(1)	–O 12	2.93(1)
–O 7	2.98(1)	–O 2	2.98(1)
–O 6	2.99(1)	–O 1	3.02(1)
–O 4	2.99(1)	–O 26	3.24(2)
–O 24	3.76(2)	–O 24	3.48(2)
–O 26	3.83(2)	–O 13	3.68(1)
K 2–O 22	2.81(2)	K 5–O 3	2.85(1)
–O 20	2.82(2)	–O 4	2.89(1)
–O 8	2.86(1)	–O 14	2.90(1)
–O 17	2.89(2)	–O 13	2.93(1)
–O 14	2.97(1)	–O 7	2.95(1)
–O 9	3.56(2)	–O 2	2.96(1)
K 3–O 18	2.80(2)	–O 10	2.99(1)
–O 11	2.85(1)	–O 15	3.13(1)
–O 3	2.90(1)	–O 22	3.27(1)
–O 19	2.93(2)	–O 21	3.81(1)
–O 10	2.98(1)		
–O 16	3.30(2)		
K 6–O 13	2.82(1)	K 8–O 6[c]	2.79(1)
–O 5	2.82(1)	–O 6[d]	2.87(1)
–O 1	2.86(1)	–O 4	2.88(1)
–O 3	2.89(1)	–O 2	2.90(1)
–O 11	3.03(1)	–O 5	2.95(1)
–O 25	3.05(1)	–O 11	3.00(1)
–O 24	3.07(1)	–O 26	3.05(1)
–O 20	3.29(1)	–O 16	3.15(1)
–O 8	3.35(1)	O 21	3.47(1)
–O 17	3.78(1)	–O 19	3.47(1)
–O 19	3.83(1)		
–O 7	3.96(1)		
K 7–O 9[e]	2.82(1)	N 1–O 1	1.25(1)
–O 12	2.88(1)	–O 2	1.25(1)
–O 9[c]	2.91(2)	N 2–O 4	1.27(1)
–O 8	2.92(1)	–O 5	1.26(1)
–O 10	2.92(1)	N 3–O 7	1.22(2)
–O 23	2.96(1)	–O 8	1.25(2)
–O 14	3.03(1)		
–O 1	3.06(1)		
–O 18	3.31(1)		
–O 17	3.77(1)		

O 1–N 1–O 2	117(1)	O 6–N 9–O 6	121(2)
O 4–N 2–O 5	115(1)	O 19–N 10–O 20	115(2)
O 7–N 3–O 8	117(2)	O 23–N 11–O 24	118(2)
O 11–N 4–O 12	116(1)	O 9–N 12–O 9	125(3)
O 17–N 5–O 18	116(3)	O 10–N 13–O 10	119(2)
O 3–N 6–O 3	115(2)	O 25–N 14–O 26	118(2)
O 15–N 7–O 16	124(3)	O 13–N 15–O 13	116(2)
O 21–N 8–O 22	122(2)	O 14–N 16–O 14	117(2)

[a] ... denotes an intramolecular, non-bonded contact. [b] Nitrogen atoms for which only one N–O distance is quoted lie on mirror planes and, therefore, there is only one independent N–O distance for those NO_2^- ions. [c] At x, y, z. [d] At 1 – x, –y, –z. [e] At –x, –y, –z.

$$\sigma(F_o^2) = 1/Lp[(I + B)^2 + (0.051)^2]^{1/2}$$

with Lp = the Lorentz and polarization factors, I is the total integrated intensity of the peak and B is the time-scaled background [25]. The final values of the positional and thermal parameters are listed in Table II and the distances and angles are listed in Table III. A table of structure amplitudes, their estimated standard deviations and the values of the calculated structure amplitudes is reproduced in Table IV. The shapes of the molecular species present in the lattice of $K_3Cu(NO_2)_5$ are shown in Figures 1–10 and a packing diagram is shown in Fig. 11.

Description of the Structure

The Environment of the Cu^{2+} Ions

Although there are four structurally independent copper species in the asymmetric unit, there are only two molecularly different entities occurring in pairs. Thus, Cu1 and Cu2 form a pair as do Cu3 and Cu4. The members of this pair have qualitative shapes which are identical to the eye; furthermore, the differences in bond lengths and angles for chemically related pairs in species 1 and 2 or 3 and 4 are of doubtful statistical significance. As a result, we felt it was unnecessary to depict the members of the pair as separate figures; instead, we labelled the central ions

TABLE IV. Structure Factors.

K	H	FO	SIG	FC
*** L= 0 ***				
0	4	4606	185	4587
0	8	10974	439	12147
0	10	869	52	1069
0	12	3671	147	3501
0	16	3828	153	3384
0	18	1154	49	1073
0	20	3275	132	3114
1	3	383	18	401
1	4	263	15	244
1	6	902	37	858
1	7	441	22	512
1	8	2586	104	2449
1	9	1781	72	1537
1	10	1987	80	1906
1	11	497	24	555
1	12	1177	48	1169
1	13	369	25	292
1	14	735	32	766
1	15	532	30	556
1	16	1570	64	1426
1	17	485	30	309
1	18	1115	47	1085
1	19	539	37	614
1	20	1858	75	1760
2	5	407	20	384
2	6	1895	76	1866
2	7	473	23	388
2	9	518	25	499
2	10	3721	149	3338
2	14	1880	75	1997
2	15	1636	66	1611
2	16	379	29	456
2	18	1385	57	1267
2	19	1527	62	1651
2	20	636	31	634
3	4	569	25	568
3	6	365	23	411
3	7	535	25	532
3	8	478	24	481
3	9	1097	45	1085
3	10	691	30	571
3	11	319	25	305
3	12	450	25	434
3	14	1118	46	1177
3	15	566	29	440
3	16	1299	53	1227
3	18	637	31	552
4	0	3811	153	3897
4	3	1030	42	1039
4	4	4981	199	5279
4	5	1594	64	1523
4	7	242	25	247
4	8	1195	49	1187
4	12	700	31	789
4	13	331	27	342
4	14	300	30	362
4	16	2757	111	2591
4	20	501	29	612
5	3	1516	61	1594
5	4	895	37	913
5	5	2232	90	2392
5	6	1480	60	1441
5	7	302	25	196
5	9	361	25	362
5	10	1430	58	1393
5	11	609	28	586
5	13	362	26	456
5	15	322	31	285
5	16	1135	47	1161
5	18	1322	54	1237
6	0	401	29	526
6	1	1877	75	1930
6	2	6649	266	7432
6	3	3302	132	3435
6	4	336	22	347
6	5	1905	77	1919
6	6	1858	75	1753
6	9	883	37	877
6	10	4776	191	4742
6	11	1944	79	1895
6	15	375	30	369
6	17	322	34	355
6	18	2280	92	2120
6	19	1800	73	1911
6	20	738	34	724
7	1	800	33	804
7	2	1466	59	1473
7	3	2215	89	2176
7	4	353	22	367
7	5	1048	43	1019
7	6	970	40	979
7	7	889	38	883
7	8	465	25	490
7	9	850	36	915
7	10	1914	77	1970

K	H	FO	SIG	FC
8	17	742	35	783
8	18	741	35	695
9	2	545	25	521
9	4	345	23	417
9	6	897	38	909
9	8	1364	56	1300
9	9	1215	53	1235
9	10	1126	47	1172
9	11	591	29	604
9	12	434	28	408
9	13	370	31	456
9	14	908	39	831
9	16	398	32	410
9	17	623	32	625
9	18	353	37	323
10	1	342	22	399
10	2	770	33	699
10	3	733	32	751
10	5	905	38	927
10	6	2609	105	2461
10	7	529	26	464
10	8	385	28	450
10	9	1208	50	1265
10	10	1957	80	1969
10	14	1955	79	1691
10	15	1378	57	1379
10	18	542	31	533
11	1	706	31	719
11	2	476	24	501
11	3	841	36	991
11	5	264	30	302
11	6	812	35	783
11	7	1135	47	1165
11	9	960	41	997
11	10	707	33	743
11	12	422	29	325
11	13	603	31	614
11	14	994	43	1020
11	16	413	29	393
12	0	1148	48	999
12	1	476	25	507
12	3	794	34	726
12	4	2964	119	2979
12	5	770	34	649
12	12	1159	49	1104
12	13	564	31	598
12	14	540	30	490
12	16	642	33	723
13	1	1330	54	1313
13	5	786	34	710
13	6	263	34	276
13	7	498	28	446
13	9	875	38	821
13	13	969	43	984
14	0	746	40	369
14	1	769	34	815
14	2	2206	89	2248
14	3	1317	54	1370
14	4	329	29	376
14	7	520	29	507
14	9	370	31	298
14	10	1209	50	1125
14	11	1173	49	1199
14	12	546	30	526
14	14	507	34	506
15	2	896	38	931
15	3	890	38	954
15	5	404	35	329
15	7	542	30	653
15	9	408	32	327
15	10	851	38	915
15	12	436	31	406
16	0	2106	85	2119
16	1	1214	50	1271
16	2	450	28	531
16	4	391	30	483
16	7	890	39	921
16	8	1583	65	1503
16	9	402	32	506
16	10	705	34	811
17	1	447	31	460
17	3	551	29	530
17	6	548	29	569
18	1	596	30	647
18	2	437	29	434
18	4	438	30	290
*** L= 1 ***				
0	7	466	24	365
0	9	1144	47	1205
0	13	1145	47	1230
0	17	1680	68	1720
0	21	881	38	902
1	2	205	12	210
1	7	1211	49	1150
1	8	1481	60	1451
1	9	407	22	416

K	H	FO	SIG	FC
2	12	433	23	450
2	14	911	38	818
2	15	324	29	356
2	16	829	36	827
2	18	738	33	740
2	20	519	29	608
3	1	304	15	291
3	2	423	19	415
3	4	319	19	262
3	5	816	34	839
3	6	432	23	386
3	7	248	34	172
3	8	631	28	644
3	9	834	37	914
3	11	953	40	974
3	12	485	25	453
3	15	462	26	553
3	16	565	28	549
3	19	320	31	403
3	20	490	29	495
4	0	334	16	332
4	1	329	16	340
4	4	1448	59	1400
4	5	406	22	407
4	6	371	26	400
4	8	1477	60	1417
4	9	959	40	968
4	10	282	25	232
4	12	584	28	490
4	13	607	29	451
4	14	388	26	365
4	16	667	31	686
4	17	876	38	910
4	18	393	28	426
4	20	550	30	530
5	1	512	23	505
5	6	912	38	891
5	7	957	40	924
5	8	306	24	204
5	10	831	36	885
5	14	1011	42	956
5	18	616	31	724
6	2	2572	103	2534
6	3	638	28	667
6	5	486	24	516
6	6	2960	119	2926
6	10	2370	95	2364
6	12	364	29	363
6	14	1724	70	1551
6	18	1054	45	1151
6	20	447	30	419
7	3	312	22	299
7	6	352	24	302
7	8	265	28	253
7	9	321	27	258
7	11	882	38	882
7	12	313	29	220
7	13	356	28	387
7	15	599	30	569
7	19	384	32	308
8	0	2566	103	2355
8	4	495	24	439
8	5	468	24	512
8	7	449	25	442
8	8	1224	50	1124
8	9	713	32	644
8	12	580	29	545
8	13	442	28	452
8	15	356	30	364
8	16	563	30	641
8	17	785	36	786
8	18	436	29	448
9	5	259	26	233
9	6	630	29	641
9	10	666	31	740
9	12	281	33	243
9	13	382	30	398
9	14	1028	43	1007
9	18	510	31	569
10	1	668	29	673
10	2	4059	163	4374
10	3	802	34	787
10	5	508	26	529
10	6	2998	120	3168
10	9	397	28	373
10	10	2911	117	2902
10	11	338	32	361
10	12	401	29	394
10	13	368	30	360
10	14	1960	79	1985
11	3	775	33	824
11	6	515	27	564
11	7	602	29	678
11	11	882	42	898
11	14	545	29	551
12	3	410	25	289

K	H	FO	SIG	FC
14	9	517	30	433
14	10	2384	96	2302
14	11	409	31	453
15	2	324	31	315
15	9	364	33	436
15	11	473	29	398
15	12	431	31	487
16	0	1244	51	1224
16	3	464	28	585
16	4	1144	48	1276
16	5	573	29	548
16	8	593	30	638
16	9	493	30	544
17	7	498	29	404
18	2	1100	46	1252
18	3	517	28	558
18	5	400	30	469
*** L= 2 ***				
0	0	3638	146	4047
0	4	5208	209	5402
0	6	484	22	468
0	8	5974	239	5895
0	12	5095	204	4855
0	14	802	35	720
0	16	3825	153	3485
1	1	515	23	526
1	4	748	31	749
1	5	439	21	455
1	6	1596	64	1565
1	7	991	41	993
1	8	955	39	867
1	9	553	25	536
1	10	568	26	500
1	11	561	26	524
1	12	1645	67	1542
1	13	241	34	252
1	14	1103	46	1058
1	16	1653	67	1569
1	18	576	29	602
2	1	473	20	472
2	5	707	30	665
2	6	4395	176	4460
2	7	1322	54	1314
2	10	3068	123	2891
2	11	1382	56	1366
2	14	2115	85	1917
2	15	854	37	723
2	16	274	32	282
2	18	931	40	991
3	2	316	18	315
3	3	350	23	306
3	4	480	23	467
3	5	331	26	280
3	7	644	28	584
3	8	1677	68	1712
3	9	326	25	299
3	10	1552	63	1572
3	11	621	28	578
3	12	551	27	615
3	13	645	29	689
3	14	587	29	612
3	15	719	32	600
3	16	376	28	337
3	18	783	35	795
3	20	750	34	863
4	0	6659	267	7633
4	3	795	33	790
4	4	3055	123	3003
4	5	665	29	617
4	7	368	24	408
4	8	6888	276	7271
4	10	704	31	731
4	12	2511	101	2541
4	13	308	28	200
4	14	380	26	378
4	16	1215	50	1186
4	17	325	31	300
4	18	629	30	698
4	20	1185	49	1385
5	1	1293	52	1343
5	2	786	33	762
5	3	338	24	322
5	4	295	23	305
5	5	376	26	336
5	6	642	29	709
5	7	1037	43	918
5	8	1067	44	989
5	9	1122	46	1171
5	10	659	30	620
5	11	601	28	512
5	12	632	30	617
5	13	582	29	705
5	14	1479	60	1436
5	16	387	28	410
5	17	341	30	369
5	18	337	31	383

K	H	FO	SIG	FC
7	3	1100	45	1143
7	4	942	39	868
7	5	444	24	365
7	6	1156	48	1120
7	7	585	35	708
7	8	502	26	523
7	10	673	31	630
7	12	942	40	947
7	14	1841	75	1732
7	16	683	32	720
7	17	383	30	362
8	0	1167	47	1114
8	3	1608	65	1613
8	4	4781	191	5226
8	5	1033	43	1130
8	6	289	26	239
8	7	381	25	395
8	8	1878	76	1934
8	9	347	27	394
8	11	501	28	454
8	12	2832	114	2776
8	14	825	36	818
8	15	309	34	369
8	16	1462	60	1429
8	17	595	31	599
9	1	630	28	726
9	3	1047	43	1101
9	5	513	26	584
9	10	707	32	714
9	11	734	33	713
9	13	1043	44	1017
9	15	484	29	537
9	16	694	33	696
9	18	359	36	437
10	0	461	23	470
10	1	693	30	734
10	2	1205	49	1113
10	3	687	30	704
10	6	732	33	660
10	7	254	33	253
10	10	2887	116	2909
10	11	2071	84	2063
10	12	360	30	311
10	16	403	29	394
11	1	420	23	411
11	2	632	29	713
11	3	234	31	269
11	5	368	26	409
11	6	327	28	355
11	7	310	31	382
11	8	286	33	321
11	9	863	38	840
11	10	1487	61	1529
11	12	419	35	384
12	0	2549	102	2307
12	1	1461	59	1484
12	2	431	26	426
12	4	1569	64	1557
12	5	554	28	611
12	7	678	32	705
12	8	1529	62	1452
12	10	683	32	663
12	11	526	31	459
12	12	543	30	507
13	2	440	25	415
13	3	400	26	378
13	6	277	34	286
13	7	382	29	338
13	8	439	28	347
13	9	859	38	790
13	14	587	33	575
14	0	551	28	521
14	5	355	29	409
14	6	1055	44	1097
14	7	1067	45	1061
14	10	450	29	392
14	13	485	31	530
15	5	785	35	776
15	6	307	33	270
16	0	502	27	394
16	3	803	36	832
16	4	1361	56	1383
16	5	486	28	434
17	1	705	32	677
17	5	450	28	407
17	6	362	31	392
17	7	482	29	477
*** L= 3 ***				
0	1	320	17	258
0	13	629	29	738
0	17	414	32	440
1	1	855	36	830
1	2	281	19	300
1	4	181	24	188
1	6	277	20	246
1	8	329	20	296

K	H	FO	SIG	FC
2	14	300	29	337
2	16	533	28	538
2	18	558	28	571
2	20	623	31	655
3	1	1269	51	1300
3	2	769	32	772
3	4	621	28	586
3	7	706	31	627
3	8	907	38	885
3	9	346	28	378
3	10	481	24	474
3	11	808	35	790
3	12	659	30	656
3	15	480	28	508
3	16	568	29	600
3	17	371	28	382
3	19	551	29	528
3	20	444	30	488
4	0	1070	44	1013
4	1	796	33	827
4	3	724	31	773
4	4	2723	109	2686
4	8	1762	71	1681
4	9	585	27	559
4	11	336	26	289
4	12	791	34	680
4	13	464	26	313
4	16	657	31	677
4	17	856	37	890
4	20	477	30	478
5	1	759	32	845
5	2	300	20	301
5	3	643	28	747
5	6	519	25	492
5	7	589	28	636
5	8	573	27	575
5	10	820	35	857
5	11	729	32	723
5	12	446	26	431
5	14	585	29	532
5	15	511	28	515
5	16	375	28	343
5	18	437	28	518
6	1	555	25	578
6	2	2639	106	2822
6	3	394	22	410
6	4	258	26	271
6	5	515	25	534
6	6	2471	99	2449
6	7	396	24	386
6	8	317	26	326
6	9	404	25	387
6	10	2175	88	2235
6	12	712	34	709
6	14	892	38	813
6	16	389	29	391
6	18	644	32	769
7	1	279	20	316
7	2	606	27	587
7	3	1541	62	1610
7	4	273	25	241
7	5	288	26	227
7	6	480	25	457
7	7	467	26	494
7	8	378	25	350
7	9	336	27	268
7	11	1699	69	1732
7	12	649	31	614
7	13	445	28	463
7	15	632	31	627
8	0	1503	61	1438
8	1	425	22	429
8	2	213	27	267
8	3	559	26	558
8	8	732	33	697
8	10	421	27	418
8	12	792	35	735
8	13	522	28	557
8	16	530	30	566
8	18	408	31	464
9	1	393	22	354
9	2	278	24	243
9	3	625	28	582
9	4	375	24	328
9	5	321	25	262
9	6	783	34	762
9	7	312	30	335
9	10	971	41	999
9	12	443	29	439
9	13	363	31	361
9	14	1073	45	1084
10	0	361	22	321
10	1	985	41	971
10	2	3019	121	3062
10	3	881	37	872
10	4	255	29	230

(All columns continued overleaf)

TABLE IV. (continued)

7	12	324	30	259
7	15	516	30	585
7	17	681	33	764
7	18	1532	63	1572
8	0	8329	334	9208
8	1	1770	71	1661
8	2	394	22	427
8	3	290	22	235
8	4	622	30	703
8	6	303	25	359
8	7	457	26	465
8	8	4282	172	4198
8	9	475	27	438
8	10	962	41	936
8	12	1359	56	1205
8	13	635	31	638
8	16	1281	53	1214

1	10	888	37	884
1	11	608	27	571
1	12	599	27	633
1	13	398	23	366
1	14	327	26	338
1	15	412	27	391
1	16	790	35	736
1	17	386	29	321
1	18	320	30	292
2	1	190	12	160
2	2	3694	148	3858
2	3	463	21	441
2	5	585	25	640
2	6	644	28	664
2	8	579	26	601
2	9	374	22	451
2	10	2661	107	2536

12	4	1130	47	1074
12	5	402	26	479
12	9	368	30	332
12	12	382	42	317
12	13	792	36	844
13	5	308	31	313
13	6	652	31	684
13	8	296	34	275
13	10	703	33	721
13	12	544	30	520
13	14	829	38	811
14	0	284	29	250
14	1	686	31	676
14	2	3071	123	3029
14	3	901	38	927
14	5	688	31	662
14	6	2598	105	2477

5	20	813	36	940
6	0	597	26	607
6	1	1788	72	1829
6	2	1336	54	1392
6	3	465	23	494
6	5	259	25	209
6	6	4858	195	4901
6	7	1591	64	1535
6	9	453	24	438
6	10	265	29	260
6	11	769	34	597
6	13	394	29	313
6	14	3643	146	3462
6	15	902	39	760
6	18	335	32	325
6	19	393	30	466
7	2	670	29	664

1	9	243	24	241
1	10	375	22	403
1	11	681	30	709
1	12	484	25	520
1	13	517	26	562
1	16	392	27	341
1	18	396	29	404
1	19	481	28	454
1	20	460	29	407
2	1	602	26	614
2	2	1434	58	1349
2	5	255	23	264
2	6	710	31	661
2	8	312	22	289
2	10	1768	71	1742
2	11	439	24	484
2	12	360	24	373

10	5	577	28	609
10	6	2479	100	2462
10	9	504	28	455
10	10	2488	100	2403
10	12	390	30	369
10	14	1766	72	1796
11	1	457	24	486
11	9	489	29	465
11	11	377	37	344
11	14	478	30	501
13	1	348	25	324
13	6	283	34	314
13	9	522	30	483
13	10	590	31	610
13	14	575	31	526
14	1	650	30	692
14	2	2260	91	2348

K	H	FO	SIG	FC
14	3	545	28	551
14	5	332	28	302
14	6	1702	69	1659
14	7	579	30	592
14	9	504	30	461
14	10	2048	83	2030
14	11	477	30	450
15	3	423	27	432
15	6	405	28	441
15	11	618	32	619
16	0	876	38	769
16	4	900	39	853
16	5	453	27	373
16	8	551	30	527
17	4	468	29	412
*** L= 4 ***				
0	2	148	30	159
0	4	437	22	555
0	8	5168	207	5294
0	12	2062	83	2116
0	16	2020	82	1874
1	1	1044	43	897
1	2	1246	51	1203
1	3	814	34	781
1	6	622	27	606
1	8	1183	43	1192
1	11	275	27	335
1	12	861	37	924
1	13	519	25	511
1	14	938	40	969
1	16	734	33	750
1	19	393	35	406
2	1	1467	59	1420
2	2	1602	65	1399
2	3	759	32	698
2	6	2959	119	2920
2	7	663	29	665
2	10	1312	54	1290
2	11	938	39	860
2	14	2636	106	2581
2	15	1547	63	1424
2	18	431	27	455
2	19	753	34	837
3	1	1199	49	1229
3	2	1018	42	1016
3	3	222	34	183
3	4	441	24	404
3	5	788	34	742
3	6	977	41	937
3	7	427	24	447
3	10	634	29	562
3	12	650	30	589
3	13	584	29	536
3	14	1785	72	1750
3	16	967	42	914
4	0	4191	168	4199
4	1	265	23	234
4	3	971	40	978
4	4	6931	277	7844
4	5	1708	69	1693
4	6	585	27	573
4	7	263	27	272
4	8	1725	70	1628
4	9	658	30	717
4	12	2132	86	2060
4	13	517	27	456
4	14	1039	43	1069
4	16	2287	92	2135
5	2	390	22	374
5	4	1310	53	1295
5	6	385	25	424
5	7	268	23	336
5	8	615	29	553
5	10	713	33	677
5	11	529	27	586
5	12	785	35	796
5	13	1267	52	1280
5	14	707	32	724
5	15	581	30	584

K	H	FO	SIG	FC
8	17	1079	46	1069
9	1	376	23	362
9	3	474	25	407
9	5	351	26	256
9	6	534	28	521
9	9	532	29	460
9	10	573	29	590
9	13	491	29	524
9	14	518	32	540
10	0	313	26	387
10	1	1046	43	1080
10	2	1657	67	1642
10	3	686	31	741
10	4	328	26	358
10	5	1021	43	1139
10	6	2871	115	2758
10	7	1218	50	1250
10	9	382	29	379
10	10	1147	43	1166
10	11	391	30	392
10	13	345	32	279
10	14	1742	71	1611
10	15	1213	51	1270
10	16	571	31	618
11	1	954	40	958
11	3	372	26	351
11	5	399	27	377
11	6	799	35	770
11	7	589	30	545
11	12	380	32	362
11	13	687	33	666
11	14	823	37	874
12	2	328	23	383
12	3	1101	46	1154
12	4	2418	97	2422
12	5	1061	44	1065
12	6	566	29	580
12	8	542	29	680
12	11	624	32	565
12	12	1233	51	1192
12	14	560	32	674
13	1	529	27	536
13	2	389	27	442
13	5	613	30	605
13	10	535	29	471
13	13	886	40	988
14	1	431	26	440
14	2	1215	50	1215
14	3	432	28	391
14	5	472	27	481
14	6	400	29	403
14	7	574	30	535
14	8	503	29	448
14	10	783	36	732
14	11	430	31	468
15	2	533	28	516
15	3	733	33	820
16	0	1744	71	1764
16	1	765	34	770
16	3	412	28	440
16	7	504	30	490
17	1	450	30	442
17	3	677	32	675
*** L= 5 ***				
0	1	231	22	149
0	3	425	21	428
0	5	613	28	690
0	9	518	26	500
0	13	769	34	733
0	17	1230	51	1242
1	2	392	22	331
1	3	875	36	884
1	4	247	23	239
1	5	461	23	519
1	7	593	27	567
1	8	584	27	568
1	9	407	24	428
1	10	805	34	751
1	16	398	28	335

K	H	FO	SIG	FC
5	11	725	33	738
5	12	830	36	781
5	14	532	29	507
5	18	574	30	576
6	1	370	22	402
6	2	2697	108	2873
6	3	556	26	538
6	5	331	27	350
6	6	2566	103	2608
6	9	396	27	400
6	10	2069	84	1998
6	11	310	31	217
6	12	639	31	610
6	14	1244	52	1104
7	1	520	25	555
7	3	512	25	563
7	7	674	31	699
7	9	296	32	269
7	11	1023	43	1022
7	12	361	31	357
7	14	404	31	329
7	15	525	30	578
8	0	413	22	465
8	5	480	26	514
8	9	550	29	541
8	10	367	29	288
8	12	449	29	467
8	13	581	30	552
8	16	384	32	462
9	3	562	27	667
9	5	661	30	694
9	6	483	28	479
9	8	322	30	306
9	10	972	42	1007
9	14	775	35	807
10	1	770	33	774
10	2	3535	142	3520
10	6	2419	97	2380
10	7	359	30	439
10	9	446	29	420
10	10	2890	116	2816
10	14	1659	68	1652
11	1	560	27	611
11	2	614	29	661
11	3	369	27	342
11	6	575	30	677
11	9	377	31	387
11	11	642	32	601
12	1	397	25	351
12	3	326	29	414
12	4	387	28	505
12	5	483	27	560
13	6	337	31	319
13	9	412	32	444
13	10	506	31	539
14	1	512	27	547
14	2	2208	89	2337
14	3	510	29	562
14	5	369	29	385
14	6	1929	78	2005
14	9	385	32	389
14	10	1744	71	1789
15	2	357	29	268
15	3	364	29	418
16	0	1733	70	1555
16	1	520	28	464
16	3	390	28	339
16	4	963	41	883
*** L= 6 ***				
0	0	1644	67	1724
0	4	4302	172	4584
0	6	476	25	464
0	8	3154	126	3119
0	10	281	30	315
0	12	3667	147	3560
0	14	687	31	699
0	16	2376	96	2265
1	1	334	24	260
1	2	467	24	499

K	H	FO	SIG	FC
4	11	419	28	331
4	12	3205	129	3071
4	16	1515	62	1406
5	5	310	35	293
5	7	1078	45	1017
5	8	682	32	689
5	9	497	28	443
5	11	542	29	511
5	12	933	40	873
5	13	601	31	619
5	14	906	39	872
5	16	471	31	450
6	0	331	28	282
6	1	562	26	539
6	2	373	25	454
6	3	597	28	596
6	6	2714	109	2645
6	7	1385	57	1359
6	14	2374	96	2251
6	15	925	40	901
7	3	365	26	359
7	4	497	27	457
7	6	916	39	895
7	7	883	40	947
7	9	449	28	489
7	12	625	31	649
7	14	1334	55	1270
8	0	885	37	870
8	1	641	29	695
8	3	523	26	497
8	4	3559	143	3758
8	8	1031	44	1021
8	9	540	29	548
8	12	2323	94	2211
8	14	532	30	530
9	5	508	28	567
9	10	632	31	653
9	13	688	33	746
10	1	298	27	302
10	2	1254	52	1301
10	3	740	33	762
10	6	959	41	860
10	7	615	31	625
10	8	432	28	440
10	9	751	34	764
10	10	2390	96	2377
10	11	1696	69	1657
11	3	355	28	340
11	5	477	28	458
11	9	956	41	969
11	10	1020	44	1018
12	0	2040	82	1934
12	1	1162	48	1214
12	2	445	26	464
12	7	717	33	748
12	8	1315	54	1293
12	10	526	31	565
12	11	505	31	513
13	5	424	28	493
13	7	449	30	418
13	9	641	32	658
14	0	440	27	485
14	6	1022	44	1054
14	7	978	42	952
*** L= 7 ***				
0	3	346	25	352
0	9	528	35	455
0	13	1215	50	1205
1	1	396	25	349
1	3	715	31	655
1	4	386	24	355
1	8	400	24	381
1	10	484	26	485
1	11	731	32	702
1	12	746	33	724
1	13	459	27	487
2	2	1600	65	1522
2	3	473	26	426
2	6	523	26	583

K	H	FO	SIG	FC
7	6	545	29	537
7	11	1040	44	1004
8	0	1291	53	1364
8	8	492	32	581
8	12	457	31	450
8	13	529	30	560
9	3	424	27	387
9	4	342	28	292
9	6	380	30	388
9	7	415	31	355
9	10	456	31	502
9	12	469	31	475
10	1	357	27	364
10	2	2379	96	2494
10	3	591	29	565
10	6	2161	87	2209
10	10	1837	75	1786
10	11	436	32	430
11	7	458	30	416
11	9	407	31	364
13	1	395	28	414
14	1	692	32	728
14	2	1777	72	1889
*** L= 8 ***				
0	0	7670	307	8321
0	4	1601	65	1488
0	8	3930	158	3857
0	10	454	28	409
0	12	1536	63	1518
1	6	239	34	216
1	8	686	32	710
1	9	647	30	639
1	10	596	29	558
1	12	559	28	560
1	13	384	28	298
2	2	633	32	570
2	6	1297	53	1381
2	10	979	41	926
2	14	1201	50	1215
3	3	317	38	302
3	5	403	29	371
3	9	406	28	398
3	12	395	28	403
4	0	1827	74	1694
4	3	580	30	594
4	4	3190	128	3232
4	5	751	34	665
4	8	766	35	815
4	12	941	40	1012
5	3	280	33	287
5	4	399	30	380
5	10	489	30	531
5	13	522	29	554
6	1	275	29	264
6	2	2266	91	2246
6	3	562	28	580
6	6	418	31	402
6	10	1938	79	1891
6	11	462	30	484
7	2	418	27	462
7	3	586	29	593
7	10	866	38	877
8	0	3223	129	3156
8	1	576	28	520
8	8	1580	65	1471
8	10	414	31	416
9	9	577	32	515
10	2	526	28	576
10	6	1244	52	1280
11	6	527	30	524
12	3	578	29	627
*** L= 9 ***				
1	1	300	33	365
1	7	804	35	775
1	8	608	29	611
1	10	360	28	334
2	2	1436	59	1275
2	7	521	27	500
2	10	959	41	877

(All columns continued on opposite page)

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 5 16   959   41   988     1 17   369   30   407     1  4   455   24   495     2  7   361   26   414     3  3   467   31   494
 5 18   965   41   906     1 18   507   28   451     1  5   600   27   560     2 10  1408   57  1343     3 11   722   33   709
 6  1   296   21   248     2  2  3045  122  2875     1  6  1042   43   996     2 12   422   28   412     4  0   310   25   375
 6  2  3446  133  3693     2  6   590   27   724     1  7  1075   44   994     2 14   350   29   426     4  4   461   31   431
 6  4   411   23   468     2  7   591   27   594     1  8   359   24   384     2 15   486   28   519     4  8   639   31   601
 6  5   661   30   693     2 10  2273   91  2248     1 10   861   37   832     2 16   422   28   435     5  3   496   29   564
 6 10  2682  103  2716     2 11   282   28   286     1 11   522   27   467     3  1   520   26   471     5  6   484   28   445
 6 11   743   34   787     2 12   398   25   331     1 12  1056   44  1032     3  2   435   27   447     5  7   385   32   358
 6 13   302   34   371     2 14   733   33   664     1 14   594   29   611     3  3   311   35   329     6  2  1294   53  1307
 6 14   630   31   701     2 16   437   27   441     1 16   980   41   942     3  5   561   28   536     6  3   444   28   452
 6 15   880   34   831     2 18   944   40   935     2  1   603   27   551     3  6   470   27   501     6  6  1333   55  1335
 6 18  1469   60  1397     3  3   492   27   462     2  2  2122   86  1904     3  7   655   31   672     7  2   384   28   397
 7  2   501   24   491     3  5   427   25   407     2  6   892   38   974     3  8   422   27   456     7  7   420   34   476
 7  3   609   27   609     3  7   474   25   532     2  7  1696   69  1701     3  9   673   31   660     8  0   591   28   564
 7  5   661   30   715     3  9   494   26   478     2  9   543   27   518     3 12   370   28   333     8  4   560   29   512
 7  6   358   25   310     3 11   974   41   947     2 10  2743  110  2664     4  4  1074   45  1009    10  1   424   28   445
 7  7   497   27   508     3 12   715   32   710     2 11  1059   44  1043     4  5   312   30   331       ***  L=  10   ***
 7  8   381   28   456     3 13   492   27   428     2 14   809   35   813     4  8   748   34   752     0  0  2475  100  2170
 7 10  1308   54  1404     4  0   327   20   254     2 15  1275   53  1181     4  9   415   28   467     0  4  3094  124  2925
 7 12   502   29   453     4  1   433   22   421     3  1   406   23   380     4 12   502   29   494     2  3   381   31   330
 7 13   955   41   981     4  4  1334   55  1244     3  6   582   28   515     5  1   547   26   514     2  6  1116   47   968
 7 14   323   34   315     4  5   489   26   557     3  7   448   26   511     5  2   277   28   260     2  7   462   28   393
 7 15   481   30   509     4  8  1022   43   971     3  8  1324   54  1341     5 10   752   36   729     4  0  2894  116  3055
 7 17   380   32   371     4  9   566   28   660     3  9   753   34   767     5 14   539   29   504     6  2   956   41   958
 7 18   971   42  1060     4 12   590   29   556     3 10   967   41   981     6  1   359   24   381
 8  0  5016  201  5158     4 13  1235   51  1135     3 12  1020   43   979     6  2  1477   60  1626
 8  1   936   39   829     4 16   374   29   391     3 15   436   29   480     6  6  1422   58  1445
 8  3   334   23   319     4 17   513   29   570     3 16   489   28   447     6  7   412   29   410
 8  4   451   25   496     5  1   238   23   197     4  0  5511  221  5980     6 10  1841   75  1787
 8  5   335   26   321     5  3   694   31   773     4  1   529   25   574     6 11   323   34   330
 8  8  2032   82  1939     5  4   497   25   450     4  4  1208   50  1194     6 14   844   38   843
 8  9   383   27   357     5  6   508   27   524     4  7   619   30   566     7  2   432   26   455
 8 10   421   23   377     5  7   475   27   463     4  8  5473  219  5482     7  3   826   36   889
 8 12   865   38   765     5 10   666   32   657     4 10   410   27   420     7  5   332   29   288
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 07/04/73 SCOPE 3    6600 B  VERS SYS27  2MAC BKT
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12.10.41.BSEND,2,OUTPUT.
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12.11.13. (55 ASSIGNED). A001312
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12.11.13.GO(TAPE1=2,TAPE20=2)
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12.12.45.EXIT
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12.12.45.MT 55*A001312 W 000000 0000 000
12.12.45.LNCT =     1254
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12.12.45.--  000.292 EC SEC
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12.12.45.--  000.990 KWH
12.12.45.--  001.822 CCU AT $1.15/CCU  (+0.45/CCU LAB OVHD)
12.12.45.--  000.000 NTAPES
12.12.45.--  001.000 LTAPES
12.12.45.--  001.000 TP DRIVES
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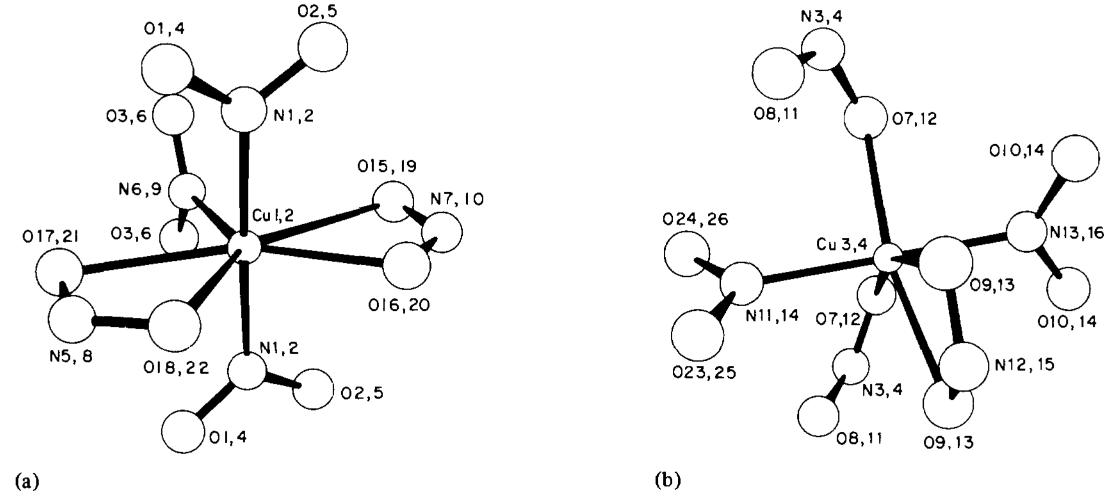

Figure 1. The shape of the coordination sphere around (a) Cu1,2 and (b) Cu3,4 and the numbering system used in labelling atoms in the crystallographic study.

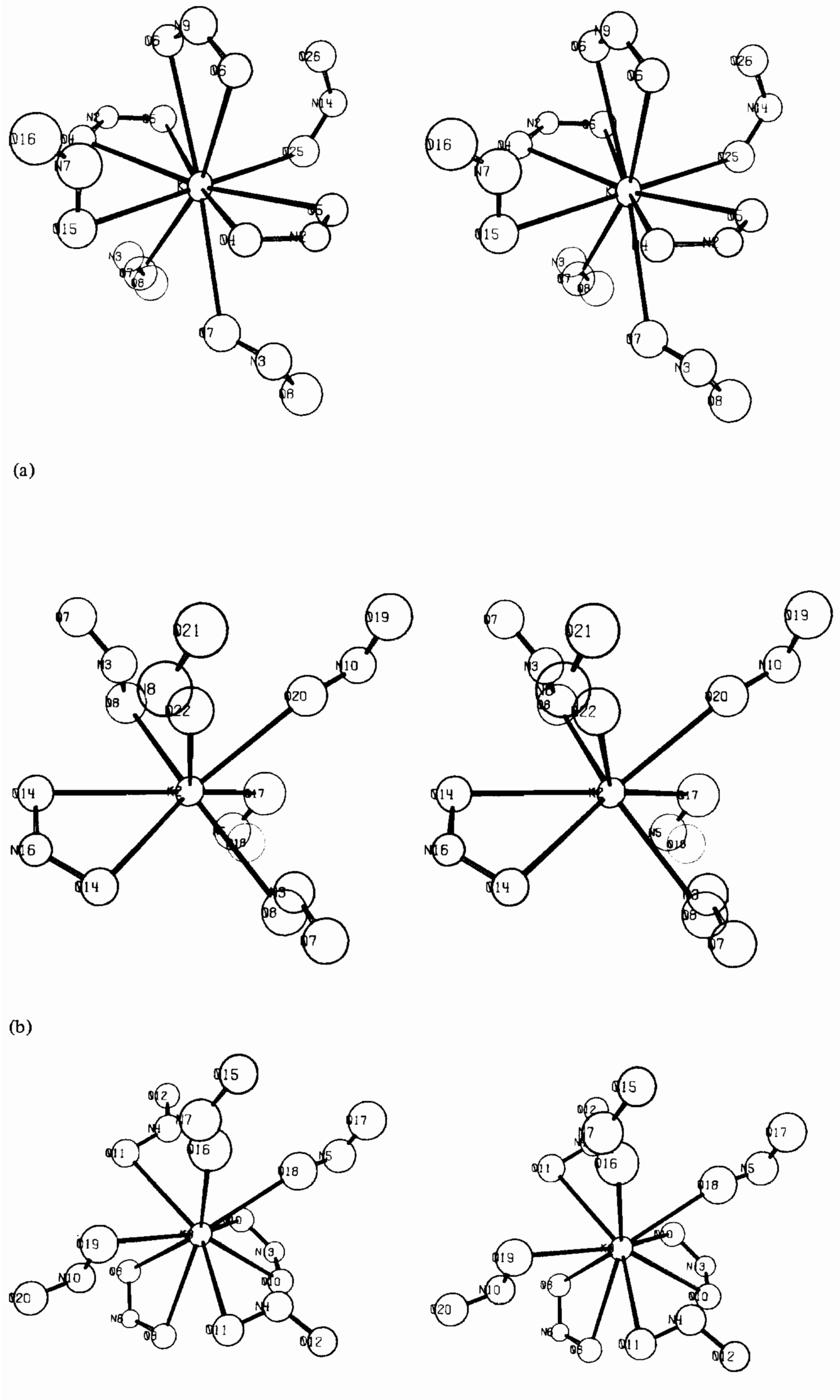

Fig. 2(a)–(c). *(For caption see page 126)*

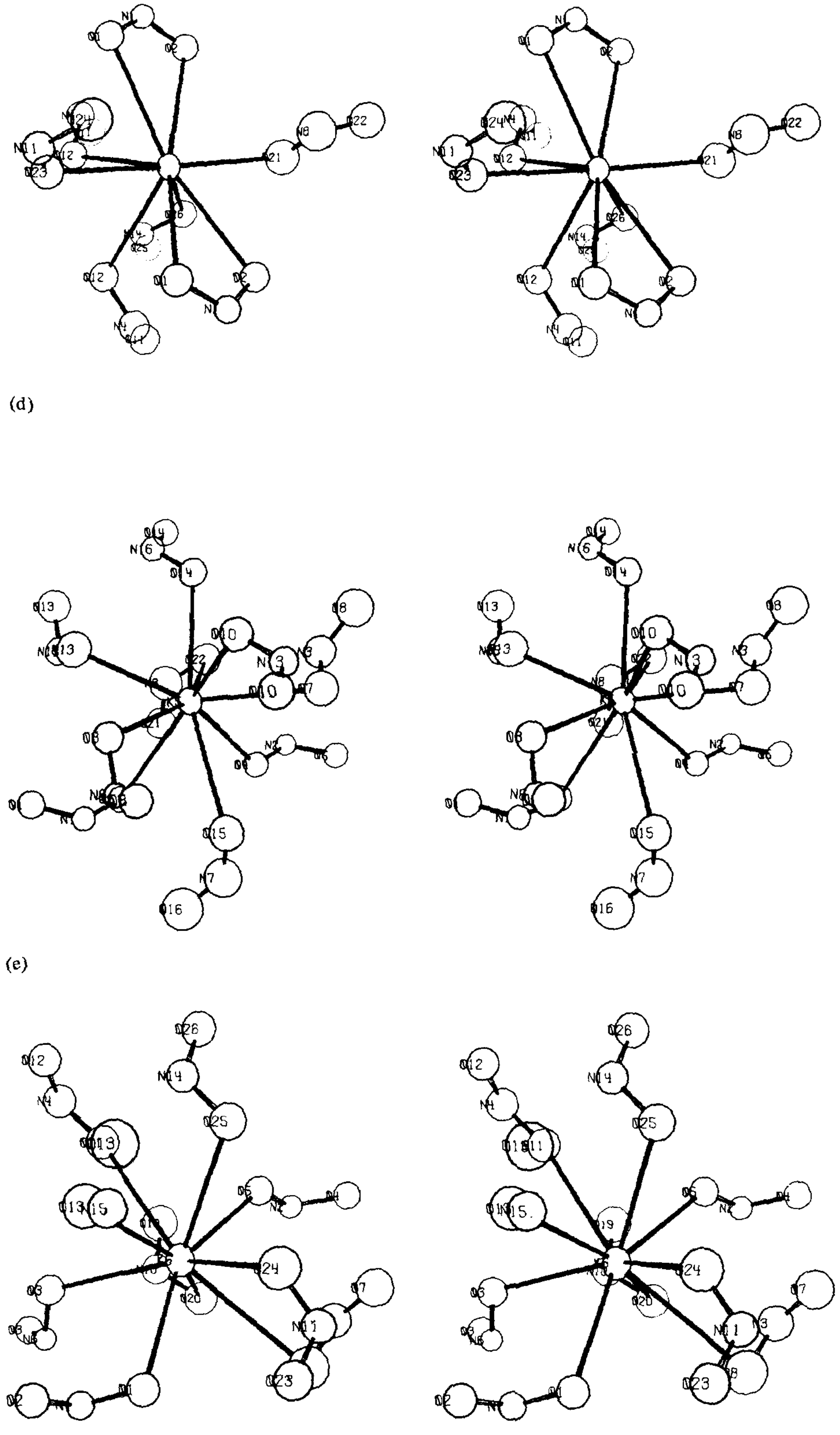

Fig. 2(a)–(f). *(For caption see page 126.)*

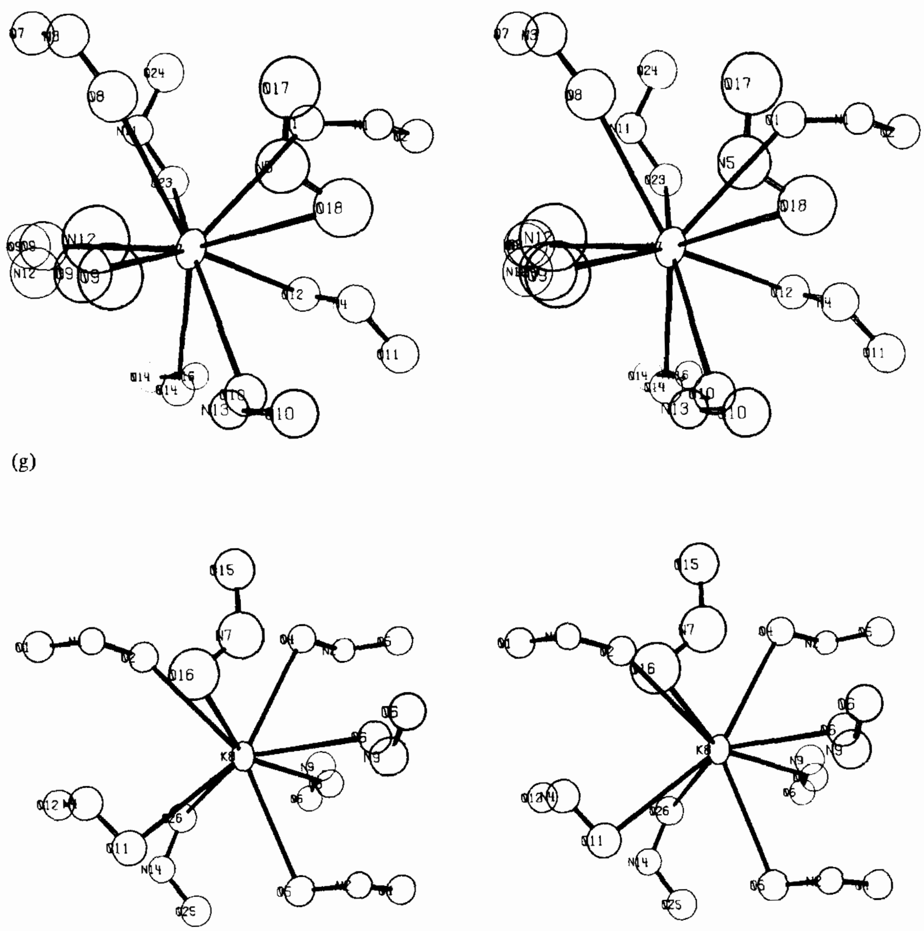

Figure 2 (a)-(h). The coordination sphere around potassium atom K1, K2, K3, K4, K5, K6, K7, K8 (according to the figure in question) and the numbering of the atoms binding the potassium atom.

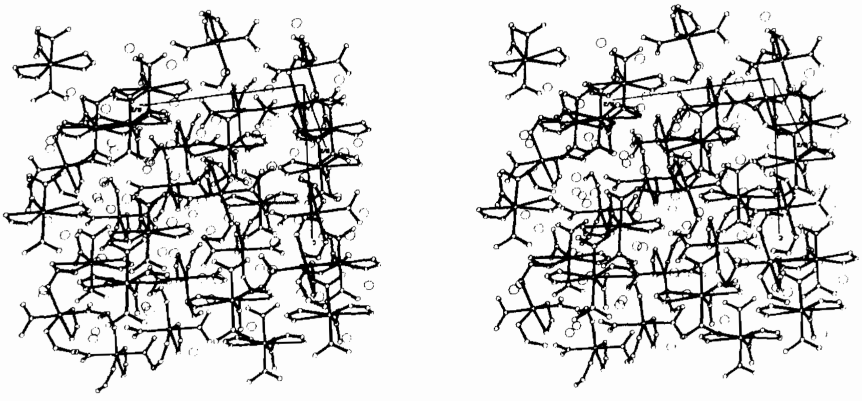

Figure 3. The packing of the cations and anions in the unit cell.

as Cu1,2 and Cu3,4. The ligands are labelled in the same way; *i.e.*, in Fig. 1, the ligands around Cu1 are O15, O16, O18, O21, N1, N6, *etc...* that is, they are the ligands with numbers between the atomic symbol and the comma separating the two sets of numbers. The two species labelled 1 and 2 (see Fig. 1) have seven ligands irregularly distributed about them [26]. The two N ligands (N1 and N2, respectively for Cu1 and Cu2) are within 2.02(1) Å of their respective Cu while the other independent nitrogen (N6, 9) is 2.08(1) Å away. The small, but significant, difference is probably due to a larger metal to ligand repulsion in the basal plane of the quasi-trigonal bipyramidal Cu moiety, as was found to be the case with CuCl$_5^{3-}$ and with CdCl$_5^{3-}$ ions [27]. Since the plane of the nitro ligands belonging to N6 and N9 (the plane of the basal nitro ligands) is nearly normal to the plane containing the Cu and the two bidentate basal ligands, the amount of ligand–ligand repulsion in the trigonal plane must be nil. Therefore, we attribute the difference in axial and equatorial Cu–N distance to an increased Coulomb repulsion between metal electrons and ligand electrons and not to either steric hindrance nor to interligand repulsions in the basal plane [27].

The oxygen ligands (O16 and O18 for Cu1) are, within experimental error, at the same bonding distance to their respective copper atoms (*i.e.*, 2.32(2) Å). The sixth and seventh ligands (O15 and O17 for Cu1) are, respectively, 2.70(2) and 2.42(2) Å away from the central ion. Similar "long bonds" were found by Wallwork and Addison [7], Duffin and Wallwork [8a] and by Duffin [8b] in anhydrous copper nitrate and other related substances. It would be easy in our case to attribute these "long bonds" to attempts by the NO$_2^-$ ligands to relieve the electronic strain imposed on the central ion by the formation of four-membered rings, CuO$_2$N, with very small O–Cu–O angles of approximately 50°; however, this is an unlikely explanation since copper species 3 and 4 contain NO$_2^-$ ligands (O9–N12–O9 for Cu3 and O13–N15–O13 for Cu4) for which the O–Cu–O angles are 51° and the two Cu–O distances are identical (by symmetry requirements) and equal to 2.35(6) Å, a value which is shorter than either of the two Cu–O bonds under consideration.

The second type of copper ion in the lattice (Cu3,4) contain two nitro ligands with Cu–N(av) distances of 2.00(2) Å which, within the stated e.s.d's are identical in length with those of the first pair of copper species (Cu1,2) despite the differences in the shapes of the coordination spheres. The two monodentate nitrito ligands (see Fig. 2) are related by a mirror plane and the unique Cu–O distance is 2.12(2) Å, which is somewhat shorter than the Cu–O distances found for the bidentate NO$_2^-$ species shown in Fig. 1. The bidentate nitrito ligand shown in Fig. 2 has two symmetrical Cu–O distances whose average value is 2.35(6) Å, which is 0.23 Å longer than those for the monodentate nitrito ligand, as expected. It is interesting to note at this point that the copper complex shown in Fig. 2 contains all the possible binding modes that an NO$_2^-$ ligand can exhibit when bound to a single central metal ion.

The Coordination Sphere Around the K Ions

There are eight crystallographically independent potassium ions in the asymmetric unit and the shape of the coordination sphere around each depends on the size of the radius we consider reasonable to accept as being within "bonding distance". The results are summarized in Table V. The results of using a cut-off radius of 3.2 Å is shown in Figs. 3–10 where the eight potassiums are shown together with their ligands and enough other atoms (N or O) to identify the NO$_2^-$ ligand in question, unless these extra atoms made the drawing too heavily overlapped. The eight independent potassiums fall into two categories depending on whether they lie at symmetry positions (mirror planes) or whether they occupy general positions of the space group. K1 through K4 lie on mirror planes and also contain one or more bidentate NO$_2^-$ ligands in their coordination sphere whereas K5 through K8 are found at general positions and are never coordinated by more than one oxygen of the NO$_2^-$ ligands. The problem in describing the coordination number and the shape of the polyhedron around each of the potassium ions is that the distances of *all* the "neighboring" oxygens for a given potassium range from 2.80 to 3.80 Å. In many ways this problem is similar to that encountered by crystallographers attempting to describe the coordination polyhedra found in alloys such as Pu$_2$Zn$_{\sim 9}$ in which Larsson and Cromer [28] state, for example, that the nearest neighbors to one of the Zn atoms (Zn(12)) are located at distances ranging from 2.546(10) Å to 3.830(10) Å. As a result, we have calculated the number of ligand atoms which are found around each potassium and present the results on Table V. As can be seen from Figs. 3 to 10, the coordination polyhedra around the potassiums do not exhibit the shapes of any of the classical polyhedra. These problems seem to be common in potassium stereochemistry; for example, Hall and Holland [10] and Power, *et al.* [11] found that the two potassiums in K$_3$Kg(NO$_2$)$_4$(NO$_3$) also have irregular coordination

TABLE V. Number of Ligands about Potassium in a Sphere of Given Radius.

	Radius		
	3.2 A	3.4 A	3.8 A
K(1)	10	10	11
K(2)	7	7	9
K(3)	8	9	9
K(4)	8	9	12
K(5)	8	9	9
K(6)	7	9	10
K(7)	8	9	10
K(8)	8	8	10

spheres with "neighboring" atom distances ranging 2.68 to 3.58 Å, values which are close to those found in this study and which present many close parallels as far as the nature of the ions and ligands concerned. Again, Larsson and Nahringbauer [29] found that the crystallographically independent potassium ion in $KH(HCO_2)_2$ contains eight oxygen nearest neighbors arranged in the form of a distorted square antiprism with K–O distances ranging from 2.773(4) to 3.059(4) Å. However, because of symmetry requirements, the potassiums in compounds of the composition $K_2BaCo(NO_2)_6$ [14] and $K_2PbCu(NO_2)_6$ [30] contain symmetrically distributed oxygen ligands. Consequently, the shape of the polyhedra around potassium ions seem to be determined primarily by packing considerations dictated by the requirements of the anions with which they are associated.

The Packing of the K^+ and $Cu(NO_2)_5^{3-}$ Ions in the Lattice

As shown above, the distribution of the individual nearest neighbor atoms to the potassiums is fairly complex; however, if one visualizes the potassium ions and the $Cu(NO_2)_5^{3-}$ anions as spheres, the packing in the lattice becomes fairly simple. In the pseudo-cubic lattice defined by 1/2a, 1/2b and c, the packing is very close to a face-centered(F) cubic lattice in which the potassiums in general positions occupy tetrahedral holes between the $Cu(NO_2)_5^{3-}$ anions while those potassiums in special positions are octahedrally surrounded by the same anions. There is a simple packing relationship between Cu1 and Cu2 ions; namely, they are related by a two-fold axis with a translation of 1/4y. This pseudo-symmetry element lies approximately at x = 1/8 and z = 1/4. The stereo pair showing the packing (Fig. 11) shows reasonably clearly the packing features described in this section.

A Comment on the Electron Spin Resonance Spectrum of $K_3Cu(NO_2)_5$

Attempts to study the esr spectrum of this substance at *room temperature* [20] gave very distorted, broad lines which were barely above the natural noise level of the Varian 4502 spectrometer. This was true irrespective of the solvent (or solvent mixture) used in the experiment although this choice was somewhat limited by the ionic nature of the compound. However, it is sufficiently soluble in methanol, DMF, diethyl ether and mixtures of these to allow preparation of solutions with concentrations normally expected to give strong signals (*i.e.*, 0.001 to 0.050 *M*). However, it was noted [20] that the esr spectra are temperature dependent in such a way as to suggest an equilibrium between two or more species and/or fluxionally equilibrated isomers. We can now easily understand the nature of this phenomenon by observing the structural details of Cu1,2 and Cu3,4. For example, if bond Cu3–O9 is broken while forming the bond Cu3–O8 (see Fig. 2), we obtain a species identical with the parent one. The reader can readily convince himself (herself) that there are four such possible pathways. Also, if we form bond Cu3–O8 (Fig. 2) while breaking bond Cu3–O7 and forming a Cu3–N3 we get the same molecule as that shown in Fig. 1. This is not unreasonable since the breaking of Cu3–O7 while forming a Cu3–N3 bond can be a simple shift of atomic positions involving no real bond breaking at that region of the molecule. The reader can easily work out a number of such rearrangements and become convinced that there is a sufficiently large number of *inter* and *intra* molecular rearrangements possible in solution to readily account for the high distortion and broadening of the solution esr spectrum.

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26 For convenience in the discussion that follows, we will use averaged values of the quantities involved since molecularly identical pairs have structural parameters which differ by no more than one or two e.s.d.'s. This should not present any problem to the reader who is referred to the tables for individual values.

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