Structure of the Potassium Salt with Dipicrylamine

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Abstract. $K^+.C_{12}H_4N_7O_{12}^-$, monoclinic, $P2_1/a$, $a = 15 \cdot 78 (2)$, $b = 13 \cdot 16 (3)$, $c = 11 \cdot 12 (2)$ Å, $\beta = 130 (1)°$, $D_m = 1 \cdot 83$, $D_c = 1 \cdot 79$ Mg m^{-3}, $Z = 4$, $M_r = 477 \cdot 32$, $\lambda(Cu\ K\alpha) = 1 \cdot 5418$ Å, $\mu(Cu\ K\alpha) = 3 \cdot 577$ mm^{-1}. The structure was solved by direct methods and refined to a final R value of $0 \cdot 1188$ with 1926 visually estimated intensities from Weissenberg photographs (H atoms not refined). Potassium ions are linked to dipicrylamine anions through oxygens in eightfold coordination. The structure is stabilized by van der Waals forces and exists in two equivalent resonating forms. The angle between two planar aromatic rings is 78° and the nitro groups are twisted out of these planes by angles varying from 8 to 34°. The average values of C=C, C—N(O), C=N and N=O are $1 \cdot 40 (2)$, $1 \cdot 46 (2)$, $1 \cdot 31 (1)$ and $1 \cdot 23 (1)$ Å respectively.

Introduction. This work was performed in connection with our systematic study on the possibility of salt formation and the structural investigation of a class of salts of dipicrylamine with organic and inorganic cations. Molecular configurations of these salts were proposed from the study on their vibrational spectra (Kundu, 1978). The structure determination of the potassium salt with dipicrylamine, which was prepared in this laboratory by treating an aqueous solution of potassium chloride with mexan (the magnesium salt with dipicrylamine), was undertaken with a view to ascertaining the mode of salt formation and the nature of bonding in the case of salts with inorganic cations. The salt is cherry red, and it melts with decomposition at 447–449 K. The single crystals of the salts were grown from aqueous solution in acetone under controlled evaporation. The crystals were thick, elongated, prismatic plates.

The single crystal used for the measurement of intensities was made approximately cylindrical with mean diameter 0·3 mm. The intensities, measured visually from Weissenberg photographs, were corrected for Lorentz–polarization and spot-shape factors and brought to an absolute scale by a statistical method (Rogers, 1965). The structure solution was first attempted by the heavy-atom technique. From a Patterson map it was found that the potassium y coordinate was zero, so that no phases could be found

for reflections with $h + k$ odd. The structure was finally solved by direct methods on an IBM 1130 computer using a combination of the programs *SIFAZ* (Chaudhuri, Mazumdar & Saha, 1978), *PAIRS* (Chaudhuri & Mazumdar, 1976) and part 4(*b*) of *SAP* (Ahmed, 1968). One of the sets of 387 phases gave an *E* map in which all the non-hydrogen atoms could be located. The first R value from the atomic positions

Table 1. *Final positional parameters* $(\times 10^4)$ *and isotropic thermal parameters with e.s.d.'s in parentheses*

	x	y	z	B_{iso} (Å^2)
K	3950 (2)	−4846 (3)	2409 (3)	1·72 (5)
C(1)	3060 (7)	−1594 (11)	4693 (11)	0·71 (17)
C(2)	4089 (8)	−2068 (11)	5312 (11)	0·92 (18)
C(3)	5089 (9)	−1881 (11)	6781 (12)	1·20 (20)
C(4)	5070 (9)	−1165 (12)	7737 (12)	1·29 (20)
C(5)	4112 (9)	−730 (12)	7285 (12)	1·16 (20)
C(6)	3146 (8)	−961 (11)	5814 (12)	1·06 (20)
C(7)	1182 (8)	−2104 (12)	2372 (12)	1·11 (19)
C(8)	741 (9)	−2789 (11)	2853 (12)	1·34 (20)
C(9)	−308 (9)	−3169 (12)	1878 (13)	1·67 (23)
C(10)	−987 (8)	−2845 (12)	319 (12)	1·33 (20)
C(11)	−667 (9)	−2202 (12)	−307 (13)	1·33 (21)
C(12)	393 (8)	−1799 (12)	734 (12)	1·23 (20)
N	2183 (7)	−1738 (10)	3202 (10)	1·34 (17)
N(1)	4133 (7)	−2836 (9)	4414 (11)	1·33 (17)
N(2)	6116 (8)	−960 (10)	9278 (11)	1·83 (20)
N(3)	2168 (7)	−463 (10)	5441 (10)	1·62 (29)
N(4)	1428 (8)	−3206 (10)	4473 (11)	2·16 (21)
N(5)	−2086 (8)	−3296 (11)	−711 (12)	2·43 (22)
N(6)	674 (7)	−1081 (10)	57 (11)	1·59 (19)
O(1)	3475 (7)	−2810 (9)	2948 (9)	2·13 (16)
O(2)	4818 (6)	−3542 (9)	5134 (10)	2·35 (18)
O(3)	6957 (7)	−1283 (9)	9587 (10)	2·87 (20)
O(4)	6090 (8)	−440 (10)	10177 (10)	3·29 (22)
O(5)	2304 (8)	169 (10)	6363 (11)	3·47 (22)
O(6)	1263 (6)	−713 (9)	4259 (11)	2·93 (20)
O(7)	2422 (7)	−3233 (10)	5272 (11)	3·14 (21)
O(8)	961 (8)	−3542 (10)	4935 (11)	3·56 (23)
O(9)	−2416 (7)	−3789 (10)	−142 (12)	3·03 (21)
O(10)	−2665 (7)	−3124 (10)	−2172 (10)	2·94 (21)
O(11)	227 (8)	−1164 (10)	−1357 (10)	3·10 (21)
O(12)	1271 (8)	−373 (9)	833 (12)	3·55 (23)
H(1)	5870	−2100	7100	1·60
H(2)	4100	−350	8110	1·56
H(3)	−630	−3600	2310	2·17
H(4)	−1250	−2000	−1500	1·83

found from this map was 0·31. The least-squares refinement with non-hydrogen atomic positional and thermal parameters on an IBM 1130 computer using a combination of the programs *MAMIE* and *BLOK* (Vickery, 1970) gave the R value 0·106 for reflections having $F_o > 10$. The H positions were determined from the difference Fourier map and the stereochemical concepts of the structure. The final R value for all the observed reflections was 0·1188. No extinction correction was made. Atomic scattering factors for C, N, O and K were taken from Cromer & Waber (1965) and those for H from Stewart, Davidson & Simpson (1965).

Table 2. *Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses*

C(1)–C(2)	1·44 (2)	C(10)–N(5)	1·46 (2)
C(2)–C(3)	1·38 (1)	C(12)–N(6)	1·44 (2)
C(3)–C(4)	1·44 (2)	N(1)–O(1)	1·25 (1)
C(4)–C(5)	1·37 (2)	N(1)–O(2)	1·25 (1)
C(5)–C(6)	1·37 (1)	N(2)–O(3)	1·22 (1)
C(1)–C(6)	1·43 (2)	N(2)–O(4)	1·23 (1)
C(7)–C(8)	1·44 (2)	N(3)–O(5)	1·23 (2)
C(8)–C(9)	1·36 (2)	N(3)–O(6)	1·21 (1)
C(9)–C(10)	1·40 (2)	N(4)–O(7)	1·21 (1)
C(10)–C(11)	1·38 (2)	N(4)–O(8)	1·22 (1)
C(11)–C(12)	1·39 (2)	N(5)–O(9)	1·23 (2)
C(7)–C(12)	1·45 (2)	N(5)–O(10)	1·27 (1)
C(1)–N	1·32 (1)	N(6)–O(11)	1·25 (1)
C(7)–N	1·31 (1)	N(6)–O(12)	1·21 (2)
C(2)–N(1)	1·45 (2)	C(3)–H(1)	1·08
C(4)–N(2)	1·45 (1)	C(5)–H(2)	1·06
C(6)–N(3)	1·47 (1)	C(9)–H(3)	1·06
C(8)–N(4)	1·49 (2)	C(11)–H(4)	1·05

C(2)–C(1)–C(6)	113 (1)	C(1)–N–C(7)	139 (1)
C(2)–C(1)–N	119 (1)	C(2)–N(1)–O(1)	121 (1)
C(6)–C(1)–N	128 (1)	C(2)–N(1)–O(2)	119 (1)
C(1)–C(2)–C(3)	125 (1)	O(1)–N(1)–O(2)	121 (1)
C(1)–C(2)–N(1)	121 (1)	C(4)–N(2)–O(3)	118 (1)
C(3)–C(2)–N(1)	114 (1)	C(4)–N(2)–O(4)	117 (1)
C(2)–C(3)–C(4)	116 (1)	O(3)–N(2)–O(4)	124 (1)
C(3)–C(4)–C(5)	123 (1)	C(6)–N(3)–O(5)	119 (1)
C(3)–C(4)–N(2)	117 (1)	C(6)–N(3)–O(6)	119 (1)
C(5)–C(4)–N(2)	120 (1)	O(5)–N(3)–O(6)	123 (1)
C(4)–C(5)–C(6)	117 (1)	C(8)–N(4)–O(7)	120 (1)
C(1)–C(6)–C(5)	125 (1)	C(8)–N(4)–O(8)	118 (1)
C(1)–C(6)–N(3)	121 (1)	O(7)–N(4)–O(8)	122 (1)
C(5)–C(6)–N(3)	113 (1)	C(10)–N(5)–O(9)	120 (1)
C(8)–C(7)–C(12)	114 (1)	C(10)–N(5)–O(10)	117 (1)
C(8)–C(7)–N	129 (1)	O(9)–N(5)–O(10)	124 (1)
C(12)–C(7)–N	117 (1)	C(12)–N(6)–O(11)	119 (1)
C(7)–C(8)–C(9)	124 (1)	C(12)–N(6)–O(12)	120 (1)
C(7)–C(8)–N(4)	122 (1)	O(11)–N(6)–O(12)	121 (1)
C(9)–C(8)–N(4)	113 (1)	C(2)–C(3)–H(1)	122
C(8)–C(9)–C(10)	116 (1)	C(4)–C(3)–H(1)	120
C(9)–C(10)–C(11)	125 (1)	C(4)–C(5)–H(2)	121
C(9)–C(10)–N(5)	115 (1)	C(6)–C(5)–H(2)	121
C(11)–C(10)–N(5)	119 (1)	C(8)–C(9)–H(3)	122
C(10)–C(11)–C(12)	117 (1)	C(10)–C(9)–H(3)	121
C(7)–C(12)–C(11)	123 (1)	C(10)–C(11)–H(4)	119
C(7)–C(12)–N(6)	122 (1)	C(12)–C(11)–H(4)	124
C(11)–C(12)–N(6)	115 (1)		

Table 3. *Intermolecular contact distances (Å) less than 3·4 Å*

|			
K(I)···N(5)(II)	3·32 (2)	N(6)(I)···O(12)(II)	3·19 (2)
K(I)···O(1)(I)	2·95 (1)	O(1)(I)···O(3)(III)	3·10 (2)
K(I)···O(2)(I)	2·94 (1)	O(1)(I)···O(5)(IV)	3·22 (2)
K(I)···O(2)(II)	2·98 (1)	O(1)(I)···H(3)(III)	2·69
K(I)···O(3)(III)	3·04 (2)	O(2)(I)···O(5)(IV)	3·11 (2)
K(I)···O(5)(IV)	3·04 (2)	O(2)(I)···O(6)(III)	3·16 (2)
K(I)···O(6)(III)	2·91 (1)	O(2)(I)···O(8)(III)	3·37 (2)
K(I)···O(9)(II)	2·76 (1)	O(3)(I)···O(9)(IV)	3·33 (2)
K(I)···O(10)(II)	3·26 (2)	O(4)(I)···O(5)(II)	2·97 (1)
K(I)···O(11)(IV)	2·83 (1)	O(4)(I)···O(9)(IV)	3·03 (2)
C(2)(I)···O(8)(III)	3·34 (2)	O(4)(I)···H(3)(IV)	3·38
C(3)(I)···O(8)(III)	3·17 (2)	O(5)(I)···O(7)(IV)	2·99 (1)
C(3)(I)···O(11)(III)	3·22 (2)	O(5)(I)···O(10)(III)	3·13 (2)
C(9)(I)···O(1)(III)	3·11 (2)	O(7)(I)···H(4)(III)	2·77
N(1)(I)···O(5)(IV)	3·20 (2)	O(8)(I)···O(10)(III)	3·30 (2)
N(1)(I)···O(8)(III)	3·13 (2)	O(8)(I)···H(1)(III)	2·64
N(1)(I)···H(3)(III)	3·21	O(9)(I)···O(11)(III)	3·03 (2)
N(2)(I)···O(9)(IV)	3·28 (2)	O(9)(I)···O(12)(III)	3·09 (2)
N(3)(I)···O(7)(IV)	3·21 (2)	O(10)(I)···H(2)(III)	3·28
N(3)(I)···O(10)(III)	3·11 (2)	O(11)(I)···H(1)(III)	3·38
N(5)(I)···O(4)(IV)	3·09 (2)	O(12)(I)···O(12)(II)	3·31 (2)
N(5)(I)···H(2)(III)	3·40	O(12)(I)···H(4)(II)	3·21
N(6)(I)···O(9)(III)	3·17 (2)	H(2)(I)···H(2)(II)	3·35
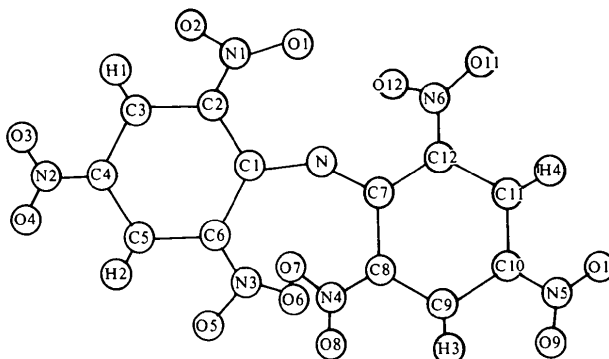
Fig. 1. Numbering of atoms.

The final atomic coordinates and thermal parameters with standard deviations are shown in Table 1.* The bond lengths and angles with their standard deviations for the final refined structure are shown in Table 2. The numbering of the atoms is shown schematically in Fig. 1. Intermolecular contact distances (less than 3·4 Å) from the atoms of the reference molecule (I) at x,y,z to the atoms of the symmetry-related neighbouring molecules at $\bar{x},\bar{y},\bar{z}$ (II), 0·5 + x, 0·5 − y, z (III) and 0·5 − x, 0·5 + y, $\bar{z}$ (IV) are listed in Table 3. A projection of the molecules viewed along the b axis is shown in Fig. 2.
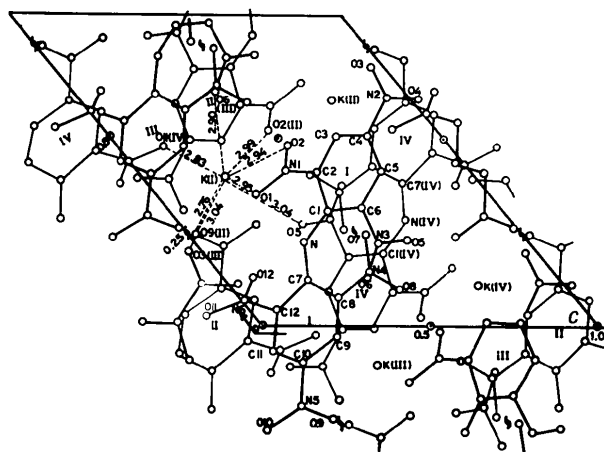

Fig. 2. View of the molecules along the *b* axis showing the close-contact distances (Å) between the potassium and dipicrylamine ions.

Discussion. It is found from Table 2 that the average C—C bond in the aromatic rings (1·40 Å) is slightly longer than that found by Cox, Cruickshank & Smith (1958) in crystalline benzene. The bond lengths C(1)—C(2) (1·44 Å), C(1)—C(6) (1·43 Å), C(7)—C(8) (1·44 Å) and C(7)—C(12) (1·45 Å) are somewhat longer than the normal value. The bond angles C(2)—C(1)—C(6) (113°) and C(8)—C(7)—C(12) (114°) are also smaller than the normal value observed in the benzene ring. The lengthening of the bonds and the narrowing of the bond angles are due to the stretching of the aromatic rings which may be a consequence of the steric hindrance and molecular packing. Similar stretching has been observed in the structure of the guanidinium salt with dipicrylamine (Gupta & Datta, 1975). The average distance between the C of the aromatic rings and the N of the nitro groups (1·46 Å) is in good agreement with the C—N distance found in polynitro aromatic structures (Carter, McPhail & Sim, 1966; Maartmann-Moe, 1969; Thewalt & Bugg, 1972). This C—N distance shows single-bond character. The bond distances C(1)—N (1·32 Å) and C(7)—N (1·31 Å), which are not significantly different, show double-bond character between C and N. The double-bond character has been determined from Pauling's relation $R = R_1 - (R_1 - R_2)[3x/(2x + 1)]$, where R is the measured bond length, R_1 the length of the single bond, R_2 the length of the double bond and x the double-bond character. In calculating double-bond character, x, the C—N single bond and C—N double bond were taken as 1·47 Å (Pauling, 1960) and 1·26 Å (Donohue, 1947), respectively. The double-bond characters of C(1)—N (44%) and C(7)—N (54%) are not significantly different from 50%. Formally, one of these should be a single bond in character. Therefore, it is reasonable to assume that the structure exists in two equivalent resonating forms

(Ph—N=Ph ↔ Ph=N—Ph). Similarly, the two N—O distances in individual nitro groups are not significantly different from each other. This suggests that the nitro groups are also in resonating forms. From the experimental measurement, the dipole moment of the potassium salt with dipicrylamine was found to be 12·3 $\times 10^{-30}$ C m, thereby suggesting a resonating structure.

The atoms in the individual aromatic rings and nitro groups are substantially planar and the two aromatic rings are not coplanar, the angle between them being 78°. All the nitro groups are twisted out of the planes of the aromatic rings by angles varying from 8 to 34°. The rotation of the nitro groups in the *ortho* positions is appreciable. This may be caused by the intramolecular steric hindrance and also by the influence of the potassium cations near the dipicrylamine anions.

It can be seen from Table 3 that none of the closest intermolecular contacts found in this structure for different types of atoms is less than the sum of the van der Waals radii (Pauling, 1960) for the atoms involved. This suggests that van der Waals forces are the main type of intermolecular interactions that stabilize the structure. The crystal structure is characterized by a high packing density, as can be seen from Fig. 2. There are eight close contact distances between the potassium cations and the dipicrylamine anions through O atoms. The K⋯O distances ranging from 2·76 to 3·04 Å agree with those usually found in potassium salts of organic acids (Shrivastava & Speakman, 1961; Larsson & Nahringbauer, 1968; Manojlović & Speakman, 1968; Maartmann-Moe, 1969). In the crystal structure, both potassium and dipicrylamine ions co-exist and the potassium is surrounded by eight neighbouring O atoms; the coordinating O atoms around the potassium may be regarded as forming a distorted square antiprism. No hydrogen bonding has been observed in the crystal structure.

From the crystal structures of the potassium and guanidinium salts with dipicrylamine it is clear that in both the cases cations are held with dipicrylamine anions by van der Waals forces. From the studies on the vibrational spectra of these salts along with some other salts of dipicrylamine with organic and inorganic cations it has been observed that the main features (the nature of the bonding and the molecular configurations) of the spectra of both types of salts are essentially similar. Therefore, it can be concluded that dipicrylamine forms salts with both organic and inorganic cations in a similar fashion, although the stereochemistries of the individual salts may be different. This class of salts may be regarded as a loose molecular complex type.

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Tris(methyl 2-methyldithiocarbazate)nickel(II) Chloride ⅓Ethanol Trihydrate

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Abstract. $[Ni\{NH_2N(CH_3)C(S)SCH_3\}_3]Cl_2.3H_2O.-0.5C_2H_5OH$, $C_9H_{24}N_6NiS_6^{2+}.2Cl^-.3H_2O.0.5C_2H_5OH$, trigonal, $R3c$, $a = b = 14.354$ (2), $c = 45.738$ (5) Å, $U = 8181$ Å^3, $D_m = 1.50$ (by flotation), $Z = 12$, $D_c = 1.499$ Mg m^{-3}, $F(000) = 3835$, $\mu(Mo\,K\alpha) = 1.369$ mm^{-1}. The structure was solved by Patterson and Fourier techniques and refined to $R = 0.0306$ by least-squares calculations. The geometry of the coordination around the Ni atom is a distorted octahedron with the ternary symmetry retained, the chromophore being NiS_3N_3 in three five-membered chelate rings. One of the two Cl atoms is surrounded octahedrally by six equivalent water molecules. The ethanol molecule, which lies on the threefold axis, shows three different degrees of disorder.

Introduction. Dithiocarbazic acid derivatives have been studied in recent years because of their biological activity (Terada, Uda, Okitsu, Kametani & Kubota, 1977; Kubota, Uda, Mori, Kametani & Terada, 1978) and because of their coordinating properties as potential polydentate ligands (Monaci, Tarli, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1980).

The present study is part of an investigation in progress in our laboratory on the complexes of the methyl ester of N-substituted dithiocarbazic acid, $R'R''NNR'''C(S)SCH_3$. Whilst only one Ni complex is formed with $NH_2NHC(S)SCH_3$ $(= L')$, $[NiL'_3]Cl_2$, two different Ni complexes of $NH_2N(CH_3)C(S)SCH_3$ $(= L)$ can be prepared with two different metal/ligand ratios, $[NiL_2Cl_2]$ and $[NiL_3]Cl_2$. Crystals of the last complex, with three ligand molecules coordinated to the metal, can be obtained only in the presence of water molecules, which are essential for the stabilization of the complex.

In order to study the coordinating properties of this