The Crystal Structure of *N*-Methylviologenium 2-Dicyanomethylene-1,1,3,3-tetracyanopropanediide, $[(CH_3 \cdot NC_5H_4 \cdot C_5H_4N \cdot CH_3)^{2+} \cdot (C_{10}N_6)^{2-}]$

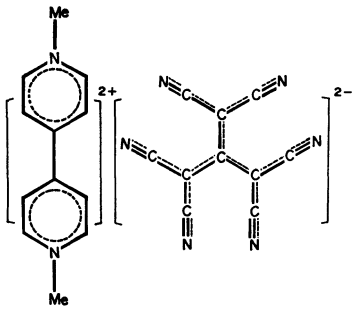
Kenichi NAKAMURA,† Yasushi KAI, Noritake YASUOKA,†† and Nobutami KASAI*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565

(Received April 13, 1981)

$[(CH_3 \cdot NC_5H_4 \cdot C_5H_4N \cdot CH_3)^{2+} \cdot (C_{10}N_6)^{2-}]$ crystallizes in the space group of $P2_1/c$, with four formula units. The unit-cell dimensions are; $a=14.625(2)$, $b=8.361(2)$, $c=17.332(3)$ Å, and $\beta=107.51(2)°$. The crystal structure was established by means of the symbolic addition method. For 2767 non-zero reflections, R is 0.074. In the crystal, divalent cations and divalent anions are stacked alternately to form infinite columns which are parallel to the b axis. Short atomic contacts are mostly involved between nitrogen atoms of the anion and carbon atoms of the cation. The $(C_{10}N_6)^{2-}$ anion takes a three-bladed propeller shape; however, it has no symmetry, unlike those in hexahydrated calcium and quinolinium salts. In the $[(CH_3 \cdot NC_5H_4 \cdot C_5H_4N \cdot CH_3)^{2+}]$ cation, two pyridine rings are twisted about the central C–C bond; the dihedral angle between the planes of two rings is 19.6(2)°.

In a series of structural studies of organic charge-transfer salts,[1–4] the crystal structure of *N*-methylviologenium 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide, $[(CH_3 \cdot NC_5H_4 \cdot C_5H_4N \cdot CH_3)^{2+} \cdot (C_{10}N_6)^{2-}]$, has been determined by means of X-ray diffraction. This salt consists of a divalent cation and a divalent anion;



Interest in the structure of the anion in this crystal has also prompted the present study in relation to the structures of the anion in the quinolinium[3] and calcium salts.[5]

Experimental

Dark-red crystals of $[(CH_3 \cdot NC_5H_4 \cdot C_5H_4N \cdot CH_3)^{2+} \cdot (C_{10}N_6)^{2-}]$ were supplied by Professor H. Mikawa and his co-workers of this university. They were recrystallized from a saturated aqueous solution by slow evaporation at room temperature. Platelet crystals elongated along the b axis were usually obtained.

The unit-cell dimensions and the integrated intensities were measured on a Rigaku automated, four-circle diffractometer, using Ni-filtered Cu $K\alpha$ radiation. The crystal data are given in Table 1. A total of 2767 independent reflections was collected by means of the θ-2θ scan technique ($2\theta \leqq 115°$). The intensities were corrected for the usual Lorentz and polarization effects, but no absorption correction was made ($\mu/cm^{-1}=6.78$ for Cu $K\alpha$).

† Present address: Energy Conversion Research Laboratory, Matsushita Electric Industrial Co., Ltd., Kadoma, Osaka 571.

†† Present address: Institute for Protein Research, Osaka University, Yamadaoka, Suita, Osaka 565.

Table 1. Crystal data of $[(CH_3 \cdot NC_5H_4 \cdot C_5H_4N \cdot CH_3)^{2+} \cdot (C_{10}N_6)^{2-}]$

$C_{22}N_8H_{14}$, *F.W.* 390.41	
Monoclinic, Space group $P2_1/c$	
a/Å	14.625(2)
b/Å	8.361(2)
c/Å	17.332(3)
β/°	107.51(2)
V/Å^3	2021.9
D_m/g cm^{-3}	1.275 (by flotation in CCl_4–CH_3OH)
Z	4
D_c/g cm^{-3}	1.283

Solution of the Structure and Refinement

The structure was solved by the symbolic-addition procedure for the centrosymmetric space group.[6] The positional and thermal parameters were refined by the block-diagonal least-squares procedure. A difference Fourier synthesis was auxiliarily used to determine the location of hydrogen atoms. The neutral atomic-scattering factors used in the calculations were taken from those given by Hanson and his co-workers.[7]

The final positional and thermal parameters of the non-hydrogen atoms are listed in Table 2, while Table 3 gives those of hydrogen atoms.†††

Calculations of the symbolic addition procedure were done with the *SSGM* program revised by one of the present authors (N.Y.). The *HBLS* IV in the *UNICS*[8] and other programs in the *UNICS*-Osaka[9] were also used. Almost all the computations were done on a FACOM 230-60 computer at Kyoto University, with the rest being done on an ACOS Series 77 NEAC System 700 computer at Osaka University.

Results and Discussion

An *ORTEP* drawing[10] of the cation and anion is shown in Fig. 1.

††† Lists of the observed and calculated structure factors and anisotropic thermal parameters are kept at the Chemical Society of Japan; Document No. 8147.

Table 2. Fractional atomic coordinates and isotropic thermal parameters of non-hydrogen atoms, with e.s.d.'s in parentheses

Atom	x	y	z	B_{eq}/Å^2
C(1)	0.0814(4)	0.1936(7)	−0.0193(3)	5.2
C(2)	0.0660(3)	0.3663(6)	0.0904(3)	4.5
C(3)	0.2182(3)	0.3117(6)	0.0815(3)	3.9
C(4)	0.2589(3)	0.3931(6)	0.1512(3)	3.6
C(5)	0.1030(3)	0.4482(6)	0.1599(3)	4.3
C(6)	0.2023(3)	0.4639(5)	0.1934(3)	3.5
C(7)	0.2452(3)	0.5468(5)	0.2714(3)	3.3
C(8)	0.1936(3)	0.5716(6)	0.3262(3)	4.1
C(9)	0.3398(3)	0.5985(6)	0.2945(3)	4.2
C(10)	0.3782(3)	0.6693(6)	0.3675(3)	4.3
C(11)	0.2349(4)	0.6429(6)	0.3986(3)	4.2
C(12)	0.3710(4)	0.7729(7)	0.4975(3)	5.6
N(1)	0.1228(3)	0.2956(5)	0.0524(2)	3.8
N(2)	0.3267(3)	0.6924(5)	0.4188(3)	4.1
C(21)	0.2183(3)	−0.1223(6)	0.1331(3)	3.6
C(22)	0.3659(3)	0.0208(6)	0.1662(3)	4.2
C(23)	0.4453(3)	0.0489(6)	0.3358(3)	4.2
C(24)	0.3334(3)	0.1902(6)	0.3879(3)	3.7
C(25)	0.1628(3)	0.0065(6)	0.3500(3)	3.6
C(26)	0.0914(3)	0.0280(6)	0.2070(3)	3.8
C(27)	0.2848(3)	−0.0250(6)	0.1904(3)	3.4
C(28)	0.3482(3)	0.0877(5)	0.3278(3)	3.3
C(29)	0.1768(3)	0.0218(6)	0.2732(3)	3.4
C(30)	0.2705(3)	0.0283(5)	0.2632(3)	3.1
N(21)	0.1692(3)	−0.2016(6)	0.0844(3)	5.1
N(22)	0.4270(3)	0.0555(7)	0.1426(3)	6.7
N(23)	0.5238(3)	0.0161(7)	0.3459(3)	6.3
N(24)	0.3246(3)	0.2762(6)	0.4369(3)	5.3
N(25)	0.1475(3)	−0.0128(5)	0.4105(3)	4.5
N(26)	0.0213(3)	0.0381(6)	0.1561(3)	5.3

Table 3. Fractional atomic coordinates and isotropic thermal parameters of hydrogen atoms, with e.s.d.'s in parentheses

Atom	x	y	z	B/Å^2
H(1A)	0.084(4)	0.064(7)	0.000(4)	6.0(15)
H(1B)	0.115(4)	0.206(7)	−0.059(3)	5.3(14)
H(1C)	0.029(4)	0.202(8)	−0.035(4)	7.4(17)
H(2)	0.000(3)	0.359(5)	0.065(3)	2.4(10)
H(3)	0.252(4)	0.266(6)	0.050(3)	3.5(11)
H(4)	0.329(3)	0.390(5)	0.172(2)	0.5(7)
H(5)	0.055(3)	0.505(6)	0.182(3)	2.6(10)
H(8)	0.127(4)	0.533(6)	0.317(3)	4.2(12)
H(9)	0.378(3)	0.595(6)	0.261(3)	3.1(11)
H(10)	0.439(3)	0.708(5)	0.380(3)	1.3(8)
H(11)	0.202(3)	0.652(6)	0.444(3)	2.9(10)
H(12A)	0.396(5)	0.885(8)	0.489(4)	8.7(19)
H(12B)	0.407(4)	0.691(8)	0.530(4)	7.1(17)
H(12C)	0.329(4)	0.791(7)	0.523(4)	6.3(15)

Structure of the $[CH_3\cdot NC_5H_4\cdot C_5H_4N\cdot CH_3]^{2+}$ *Cation.* The skeleton of the cation, together with the bond lengths and bond angles, is illustrated in Fig. 2(a). Each pyridine ring is approximately planar (Table 4). These two rings are twisted about the C(6)–C(7) bond, the dihedral angle between the planes of two rings being 19.6(2)°. The methyl carbon, C(1), attached to the N(1) atom is considerably displaced (0.14 Å) from the (1) ring plane, whereas

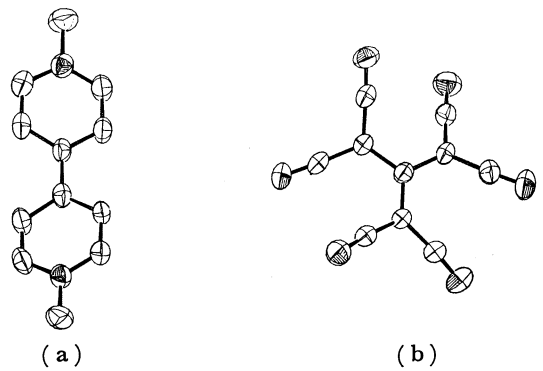


Fig. 1. A perspective view of the cation(a) and anion (b). Non-hydrogen atoms are drawn by thermal ellipsoids with 50% probability level.

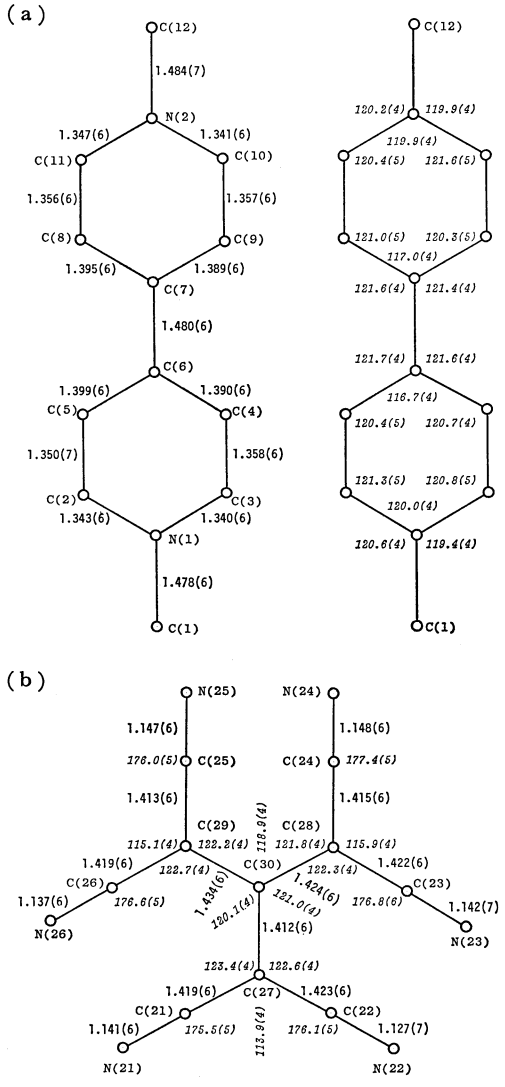


Fig. 2. Bond lengths (l/Å) and bond angles (ϕ/°) in the cation(a) and anion(b) with e.s.d.'s in parentheses.

TABLE 4. LEAST-SQUARES PLANES AND DIHEDRAL ANGLES

Least-squares planes	$AX+BY+CZ+D=0$, where $X=ax+cz\cdot\cos\beta$, $Y=by$, and $Z=cz\cdot\sin\beta$							
	A/Å	B/Å	C/Å	D/Å	Displacement of atoms from the plane (l/Å)			
$(CH_3\cdot NC_5H_4\cdot C_5H_4N\cdot CH_3)^{2+}$ ion:								
(1) Pyridine ring 1	−0.1340	−0.8389	0.5275	1.8375	N(1)	−0.010	C(4)	−0.002
					C(2)	−0.010	C(5)	0.009
					C(3)	−0.003	C(6)	0.017
(2) Pyridine ring 2	0.1812	−0.8925	0.4131	1.8331	N(2)	−0.004	C(9)	−0.000
					C(7)	−0.001	C(10)	0.003
					C(8)	−0.001	C(11)	0.003
$(C_{10}N_6)^{2-}$ ion:								
(3) Plane defined by C(27), C(28), C(29), and C(30)	−0.0762	0.9234	−0.3761	1.6176	C(27)	−0.001	C(29)	−0.001
					C(28)	−0.001	C(30)	0.003
(4) Plane defined by C(21), C(22), C(27), N(21), and N(22)	−0.3813	0.8153	−0.4359	2.7534	C(21)	0.008	N(21)	−0.005
					C(22)	−0.012	N(22)	0.007
					C(27)	0.001		
(5) Plane Defined by C(23), C(24), C(28), N(23), and N(24)	0.2540	0.7900	−0.5580	1.5843	C(23)	0.020	N(23)	−0.012
					C(24)	−0.013	N(24)	0.006
					C(28)	−0.001		
(6) Plane defined by C(25), C(26), C(29), N(25), and N(26)	0.0430	−0.9940	−0.1006	0.5878	C(25)	−0.025	N(25)	0.012
					C(26)	0.022	N(26)	−0.010
					C(29)	0.002		

Dihedral angles (ϕ/°) and angles between vectors and planes (ϕ/°)	
Dihedral angles between the (1) and (2) planes	19.6(2)
between the (3) and (4) planes	18.9(2)
between the (3) and (5) planes	23.1(2)
between the (3) and (6) planes	27.9(2)
Angles between N(1)-C(1) vector and the (1) plane	4.7
N(2)-C(12) vector and the (2) plane	1.7

the deviation of C(12), attached to the N(2) atom, from the (2) plane is only 0.02 Å. This significant displacement of the methyl carbon, C(1), from the (1) ring plane probably depends upon the strong interaction between the cation and the anion. The structure of the same cation in the crystal of $[(CH_3\cdot NC_5H_4\cdot C_5H_4N\cdot CH_3)^{2+}\cdot(CuCl_4)^{2-}]$ has previously been reported;[11] in this structure two pyridine rings and two methyl carbons attached to the respective rings are all coplanar within the range of experimental error. However, in the present complex, the cations are considerably distorted, as has been mentioned above.

Structure of the $(C_{10}N_6)^{2-}$ Anion. The bond lengths and bond angles in the anion are also given in Fig. 2(b). The four central carbon atoms, C(27), C(28), C(29), and C(30), are coplanar (Table 4), while three dicyano-substituted carbon groups, $-C(CN)_2$, are tilted out of this plane; the tilt angle are 18.9(2), 23.1(2), and 27.9(2)° respectively (Table 4). The $(C_{10}N_6)^{2-}$ anion has a C_3-3 (or approximately D_3-32) symmetry in hexahydrated calcium salt[4] and a C_2-2 symmetry in quinolinium salt,[5] whereas in the present salt the anion has no symmetry. However, there is no considerable difference in the corresponding bond lengths and bond angles in these three salts.

Crystal Structure. The crystal structure as viewed along the b and a axes is shown in Figs. 3 and 4 respectively. The crystal consists of infinite columns parallel to the b axis. In the column the divalent cations and the divalent anions are stacked alternately. They lie roughly on the (022) plane. This

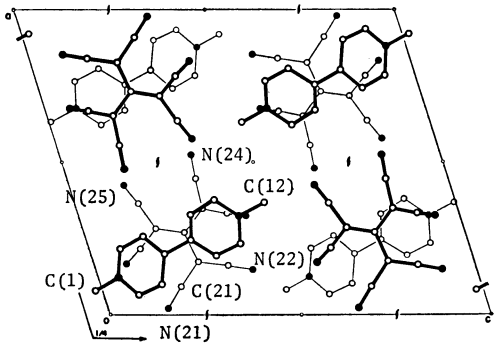


Fig. 3. Crystal structure projected along the b axis.

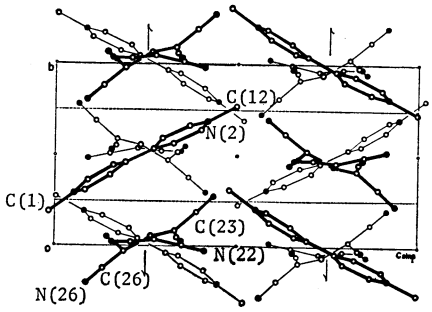


Fig. 4. Crystal structure projected along the a axis.

Table 5. Intermolecular atomic contacts (l/Å) less than 3.4 Å

1.	Cation(x, y, z) to anion(x, y, z)	
	C(2)···N(26)	3.115(7)
	C(3)···C(22)	3.290(7)
	C(3)···C(27)	3.367(6)
	C(8)···N(24)	3.353(6)
	C(11)···N(24)	3.322(6)
2.	Cation(x, y, z) to anion($x, 1+y, z$)	
	C(6)···N(21)	3.328(6)
	C(11)···C(25)	3.245(6)
	C(11)···N(25)	3.182(6)
3.	Cation(x, y, z) to anion($x, 0.5-y, -0.5+z$)	
	C(1)···N(25)	3.200(7)
	C(3)···N(25)	3.291(6)
4.	Cation(x, y, z) to anion($\bar{x}, \bar{y}, \bar{z}$)	
	C(1)···N(26)	3.080(7)
5.	Cation(x, y, z) to anion($1-x, 1-y, 1-z$)	
	C(12)···N(23)	3.214(7)
6.	Cation(x, y, z) to anion($\bar{x}, 0.5+y, 0.5-z$)	
	C(2)···N(25)	3.278(6)
	C(8)···N(26)	3.261(6)
7.	Cation(x, y, z) to anion($1-x, 0.5+y, 0.5-z$)	
	C(4)···N(23)	3.327(7)
	C(9)···N(22)	3.272(7)
	C(10)···N(22)	3.058(7)

structure well explains the particularly strong intensity of the 022 reflection. Short atomic contacts (less than 3.4 Å) between the cation and anion are listed in Table 5. Most of them are between electronegative nitrogen atoms of the anion and electropositive carbon atoms of the cation.

The authors wish to express their deep thanks to Professor Hiroshi Mikawa for the supply of crystals and for his helpful discussions. Thanks are also due to Mr. Takashi Mizuma for his help in the *ORTEP* drawings.

References

1) S. Sakanoue, Y. Kai, N. Yasuoka, N. Kasai, and M. Kakudo, *Bull. Chem. Soc. Jpn.*, **43**, 1306 (1970).
2) K. Nakamura, N. Yasuoka, N. Kasai, and M. Kakudo, *J. Chem. Soc., Chem. Commun.*, **1970**, 1135.
3) S. Sakanoue, N. Yasuoka, N. Kasai, and M. Kakudo, *Bull. Chem. Soc. Jpn.*, **44**, 1 (1971).
4) T. Tamamura, T. Yamane, N. Yasuoka, and N. Kasai, *Bull. Chem. Soc. Jpn.*, **47**, 832 (1974).
5) D. A. Bekoe, P. K. Gantzel, and N. K. Trueblood, *Acta Crystallogr.*, **22**, 657 (1967).
6) I. L. Karle, K. Britta, and P. Gum, *Acta Crystallogr.*, **17**, 496 (1964).
7) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).
8) "Universal Crystallographic Computing System," ed by T. Sakurai, The Crystallographic Society of Japan (1967).
9) "Universal Crystallographic Computing System-Osaka," The Computation Center, Osaka University (1973).
10) C. K. Johnson, *ORTEP* II, Oak Ridge National Laboratory, Tennessee (1974).
11) J. H. Russel and S. C. Wallwork, *Acta Crystallogr., Sect. B*, **25**, 1961 (1969).