

Table 8. *Ionic and van der Waals radii (Å)*

Na <sup>+</sup>	0.97	} <i>Handbook of Chemistry and Physics</i> (1977)
K <sup>+</sup>	1.33	
O	1.40	

corners of a somewhat distorted trigonal prism, the seventh O atom being located on the normal to one of the side faces. An eighth O atom, O(5) of the bidentate ligand (Fig. 2), is at 3.169 Å from K<sup>+</sup>, which represents an elongation of ~10% with respect to the other seven K—O distances, and probably still contributes to a smaller extent to the bonding.

4NO<sub>2</sub> (Estaban-Calderón *et al.*, 1982), considered as an anion, carries additional neutral donor sites, so that as a ligand it becomes more powerful and acts as a charge neutralizer as well as serving to satisfy the cationic coordination requirements. Moreover, the charge of this mononegative anion is distributed through delocalization of its bonds (Fig. 3), producing an increase of its capability as a ligand. On the other hand, the general rule that the cation–anion interaction increases with the charge density of the cation (Poonia & Bajaj, 1979) is clearly observed in 4NO<sub>2</sub>-NA and 4NO<sub>2</sub>-K. In fact, Na<sup>+</sup> is surrounded by four anionic sites (Fig. 1), whereas K<sup>+</sup> is bonded to five anionic sites (Fig. 2), and in both cases Na<sup>+</sup> and K<sup>+</sup> neutralize the same negative total charge. From this, one can deduce a higher intensity of interaction in Na—O than in K—O bonds, which can be evaluated in terms of the observed Na—O and K—O bond lengths. In fact, taking the ionic and van der Waals radii given in Table 8, and assuming an interaction model of cation–dipole type, the following expected distances are obtained: Na<sup>+</sup>—O = 2.37, K<sup>+</sup>—O = 2.73 Å. The mean distance between the cation and anion sites observed in 4NO<sub>2</sub>-NA only exceeds the expected value by 0.8%, whereas in 4NO<sub>2</sub>-K the mean observed values are elongated 6.8% with respect to the expected ones. These observations can be connected with the different cationic changeability presented by 4NO<sub>2</sub>-NA and 4NO<sub>2</sub>-K, as

mentioned above. However, it still remains unclear whether this different behaviour is a consequence of the fact that Na<sup>+</sup> interacts strongly with the bidentate ligand, with two identical short Na—O bonds, which is not observed in the case of the K<sup>+</sup> ion (Figs. 1 and 2).

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#### References

- ABRAHAMSON, S. C. & KEVE, E. T. (1971). *Acta Cryst.* **A27**, 157–165.
- BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- CABEZUELO, M. D., CANO, F. H., FOCES-FOCES, C. & GARCÍA-BLANCO, S. (1977). *Acta Cryst.* **B33**, 3598–3601.
- CANO, F. H., FOCES-FOCES, C. & GARCÍA-BLANCO, S. (1977). *Tetrahedron*, **33**, 797–802.
- ESTEBAN-CALDERÓN, C., MARTÍNEZ-RIPOLL, M. & GARCÍA-BLANCO, S. (1982). *Acta Cryst.* **B38**, 1340–1342.
- GOYA, P., MARTÍNEZ, P., OCHOA, C. & STUD, M. (1981). *J. Heterocycl. Chem.* In the press.
- GOYA, P. & STUD, M. (1978). *J. Heterocycl. Chem.* **15**, 253–256.
- Handbook of Chemistry and Physics* (1977). 57th ed., p. F-213. Ohio: CRC Press.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 72–98. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- LINNETT, J. W. (1966). *The Electron Structure of Molecules. A New Approach*. London: Methuen.
- NARDELLI, M., MUSATTI, A., DOMIANO, P. & ANDRETTI, G. (1965). *Ric. Sci.* **35**, 807–810.
- POONIA, S. N. & BAJAJ, V. A. (1979). *Chem. Rev.* **79**, 389–445.
- RICH, A. & DAVIDSON, N. (1968). *Structural Chemistry and Molecular Biology*, p. 459. San Francisco: Freeman.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

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## 4-Cyano-3-hydroxy-6H-1,2,6-thiadiazine 1,1-Dioxide: Sodium and Potassium Salts

BY C. ESTEBAN-CALDERÓN, M. MARTÍNEZ-RIPOLL AND S. GARCÍA-BLANCO

*Departamento de Rayos X, Instituto Rocasolano, CSIC, Serrano 119, Madrid-6, Spain*

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#### Abstract

These compounds belong to a series of *S*-dioxo analogs of pyrimidines synthesized as potential antimetab-

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olites. C<sub>4</sub>H<sub>2</sub>N<sub>3</sub>O<sub>3</sub>S<sup>-</sup>·Na<sup>+</sup>·2H<sub>2</sub>O has been refined to *R* = 0.035 with 2672 independent reflexions; triclinic, space group *P* $\bar{1}$  with *Z* = 2, *a* = 10.384 (1), *b* = 7.138 (1), *c* = 6.305 (1) Å,  $\alpha$  = 108.65 (1),  $\beta$  =

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102.37 (1),  $\gamma = 95.63 (1)^\circ$ . The refinement for  $C_4H_2N_3O_3S \cdot K^+ \cdot H_2O$  led to  $R = 0.042$  for 2835 reflexions; triclinic, space group  $P\bar{1}$  with  $Z = 2$ ,  $a = 9.811 (1)$ ,  $b = 7.296 (1)$ ,  $c = 5.858 (1) \text{ \AA}$ ,  $\alpha = 103.06 (1)$ ,  $\beta = 94.56 (2)$ ,  $\gamma = 100.51 (2)^\circ$ . The anion, formed by deprotonation of the hydroxy group of the title compound, behaves as a monodentate ligand for  $K^+$  ions, the potassium salt being readily able to release the free heterocycle. The sodium salt, however, presents a very low cation exchangeability. The anion seems to act to some extent as a bidentate ligand for the  $Na^+$  ions, as the cation is indirectly bonded to the bidentate ligand through a water molecule. The  $Na^+$  ions are octahedrally coordinated with distances between 2.35 and 2.54  $\text{\AA}$ , while the  $K^+$  ions are surrounded by seven neighbours at distances 2.75–2.93  $\text{\AA}$  forming a pentagonal bipyramid. The observed Na–O,–N distances agree with an interaction model of cation–dipole type better than do the somewhat elongated K–O,–N distances. The thiadiazine rings show strong electron modifications when compared with the free heterocyclic compound. Structural comparison of the present sodium compound with the 4-nitro-substituted sodium salt may in part explain the different cation exchangeability of both sodium salts. As reported in the 4-nitro-substituted salts, a proton migration occurs in the formation of the present 4-cyano salts, and dimeric anions are also formed through centrosymmetric hydrogen bonds.

### Introduction

In the course of the preparation of some 4-substituted 1,2,6-thiadiazine 1,1-dioxides (Goya & Stud, 1978), it was found that some of these compounds show a great tendency to bind alkaline ions. Thus, 3-hydroxy-4-nitro-6*H*-1,2,6-thiadiazine 1,1-dioxide (hereafter abbreviated to 4NO2; Esteban-Calderón, Martínez-Ripoll & García-Blanco, 1982*a*) binds  $Na^+$  ions giving rise to 4NO2-NA (Esteban-Calderón, Martínez-Ripoll & García-Blanco, 1982*b*) and neither acid treatment nor resin exchange can release 4NO2. However, the  $K^+$  ions in 4NO2-K (Esteban-Calderón *et al.*, 1982*b*) can be exchanged to give the free heterocyclic compound 4NO2. Similar retention capability for  $Na^+$  ions has been found (Goya & Stud, 1978) for 4-cyano-3-hydroxy-6*H*-1,2,6-thiadiazine 1,1-dioxide (4CN, Esteban-Calderón, Martínez-Ripoll & García-Blanco, 1979).

We report here the crystal structures of the sodium salt of 4CN dihydrate (4CN-NA) and of the potassium salt monohydrate (4CN-K). 4CN-NA shows a very low cation exchangeability, whereas 4CN-K can release 4CN.

### Experimental

4CN-NA and 4CN-K were crystallized from aqueous solutions as colourless, transparent single crystals.

Precise cell parameters as given in the *Abstract* were obtained as described in 4NO2 (Esteban-Calderón *et al.*, 1982*a*) with 30 reflexions. Other crystal data for 4CN-NA (and 4CN-K) are:  $D_c = 1.80 \text{ Mg m}^{-3}$  ( $1.91 \text{ Mg m}^{-3}$ ), crystal dimensions  $0.24 \times 0.29 \times 0.35 \text{ mm}$  ( $0.18 \times 0.21 \times 0.23 \text{ mm}$ ),  $\mu = 0.434 \text{ mm}^{-1}$  ( $0.898 \text{ mm}^{-1}$ ) for  $\lambda = 0.71069 \text{ \AA}$ ,  $\theta$  limits  $2\text{--}32^\circ$  ( $2\text{--}35^\circ$ ), number of unique reflexions collected: 2979 (3525), observed reflexions with  $I > 2\sigma(I)$ : 2672 (2835). The data

Table 1. Atomic coordinates and isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ ) for 4CN-NA

$$U_{eq} = \frac{1}{3} \sum_i \sum_j a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j).$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
S	0.80659 (2)	0.28548 (3)	0.37824 (4)	22
C(1)	0.69744 (10)	0.41034 (18)	0.70909 (18)	31
C(2)	0.57123 (9)	0.30297 (15)	0.58288 (16)	24
C(3)	0.54346 (9)	0.18242 (14)	0.34263 (16)	23
C(4)	0.46307 (10)	0.30646 (17)	0.68839 (18)	29
N(1)	0.80673 (10)	0.41677 (19)	0.63336 (19)	39
N(2)	0.64932 (8)	0.17656 (15)	0.24353 (15)	28
N(3)	0.37342 (11)	0.30370 (21)	0.76757 (21)	41
O(1)	0.88564 (8)	0.13125 (13)	0.38194 (16)	31
O(2)	0.84933 (10)	0.41190 (15)	0.26005 (19)	37
O(3)	0.43127 (8)	0.08588 (15)	0.22157 (14)	34
O(4)	0.16728 (8)	0.07308 (15)	0.25262 (16)	33
O(5)	0.04213 (9)	0.25437 (14)	0.94854 (15)	32
Na	0.12699 (5)	0.22204 (7)	0.62360 (8)	29
				<i>U</i>
H(C1)	0.711 (2)	0.486 (4)	0.864 (4)	24 (5)
H(N2)	0.630 (2)	0.101 (3)	0.101 (4)	18 (4)
H1(O4)	0.252 (3)	0.079 (4)	0.260 (5)	35 (6)
H2(O4)	0.141 (3)	0.126 (5)	0.150 (6)	40 (7)
H1(O5)	−0.031 (3)	0.183 (5)	0.888 (5)	34 (6)
H2(O5)	0.033 (3)	0.351 (5)	1.044 (6)	42 (7)

Table 2. Atomic coordinates and isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ ) for 4CN-K

$$U_{eq} = \frac{1}{3} \sum_i \sum_j a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j).$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
S	0.19327 (3)	0.20481 (5)	0.68985 (6)	24
C(1)	0.31636 (16)	0.06106 (22)	0.35545 (26)	29
C(2)	0.43943 (14)	0.19578 (19)	0.43323 (23)	24
C(3)	0.46465 (13)	0.32188 (18)	0.66597 (23)	22
C(4)	0.55164 (15)	0.20108 (21)	0.29456 (25)	28
N(1)	0.20404 (14)	0.03859 (20)	0.46725 (25)	33
N(2)	0.35620 (12)	0.30976 (18)	0.79974 (21)	26
N(3)	0.64513 (18)	0.20840 (27)	0.18777 (31)	42
O(1)	0.13105 (13)	0.12507 (19)	0.86912 (23)	36
O(2)	0.12478 (14)	0.34265 (21)	0.61433 (27)	39
O(3)	0.57834 (11)	0.43114 (17)	0.75232 (20)	30
O(4)	0.85499 (13)	0.38514 (21)	0.77485 (31)	41
K	0.94745 (4)	0.28567 (5)	0.18821 (7)	36
				<i>U</i>
H(C1)	0.310 (4)	−0.030 (5)	0.205 (6)	26 (7)
H(N2)	0.368 (2)	0.382 (3)	0.934 (4)	13 (4)
H1(O4)	0.771 (4)	0.389 (6)	0.739 (7)	39 (9)
H2(O4)	0.858 (7)	0.267 (10)	0.674 (11)	56 (16)

collection and intensity reduction to  $F_{rel}$  values were performed as described for 4NO<sub>2</sub>. The structure determinations and weighted refinements were done as described previously in related compounds (Esteban-Calderón *et al.*, 1982*b*). The final unweighted and weighted disagreement indices are  $R = 0.035$ ,  $R_w = 0.035$  (4CN-NA) and  $R = 0.042$ ,  $R_w = 0.049$  (4CN-K). The atomic parameters are shown in Tables 1 and 2 respectively.\*

### Description and discussion of the structures

Partial views of the crystal structures of 4CN-NA and 4CN-K are shown in Figs. 1 and 2 respectively, where several symmetrically related atoms are also shown for clarity. Hydrogen bonds are represented by dashed lines.

\* Lists of coefficients for the weighting schemes, structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36461 (48 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

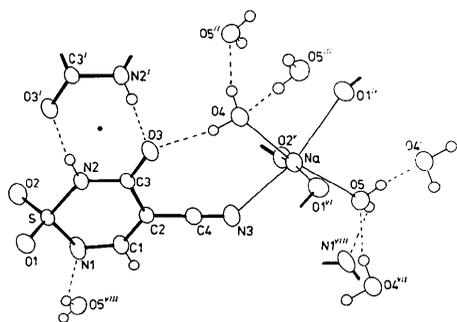


Fig. 1. Perspective drawing (Johnson, 1965) of 4CN-NA. Some symmetrically related atoms are also shown. Dashed lines represent hydrogen bonds. For symmetry operations see Table 3. Thermal ellipsoids scaled to 50% probability.

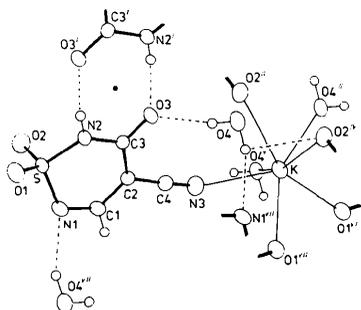


Fig. 2. Perspective drawing (Johnson, 1965) of 4CN-K. Some symmetrically related atoms are also shown. Dashed lines represent hydrogen bonds. For symmetry operations see Table 3. Thermal ellipsoids scaled to 50% probability.

Table 3. Intermolecular contacts with e.s.d.'s in parentheses

X—H...Y	X...Y	X—H	H...Y	X—H...Y
Hydrogen bonds for 4CN-NA				
O(4)—H(1)...O(3)	2.784 (1) Å	0.87 (3) Å	1.93 (3) Å	171 (3)°
O(4)—H(2)...O(5 <sup>ll</sup> )	2.809 (2)	0.86 (4)	1.97 (4)	166 (4)
O(5)—H(1)...O(4 <sup>lll</sup> )	2.780 (1)	0.82 (3)	2.01 (3)	158 (3)
O(5)—H(2)...N(1 <sup>vlll</sup> )	2.910 (1)	0.79 (4)	2.35 (3)	130 (3)
N(2)—H...O(3 <sup>l</sup> )	2.817 (1)	0.86 (2)	1.96 (2)	156 (2)
Hydrogen bonds for 4CN-K				
N(2)—H...O(3 <sup>l</sup> )	2.814 (2) Å	0.83 (2) Å	1.99 (2) Å	173 (2)°
O(4)—H(1)...O(3)	2.791 (2)	0.85 (4)	1.97 (4)	164 (4)
*O(4)—H(2)...O(2 <sup>lv</sup> )	2.924 (2)	0.94 (6)	2.64 (6)	98 (6)
*O(4)—H(2)...N(1 <sup>vll</sup> )	3.023 (2)	0.94 (6)	2.15 (6)	155 (6)
Other contacts for 4CN-NA				
O(4)—H(2)...H(2)—O(5 <sup>ll</sup> )	2.24 (6) Å			
O(4)—H(2)...H(1)—O(5 <sup>lll</sup> )	2.29 (5)			
O(4)—H(2)...H(1)—O(5 <sup>ll</sup> )	2.33 (5)			
O(5)—H(2)...O(2 <sup>vlll</sup> )	2.56 (4)			
N(3)...H—C(1 <sup>vlll</sup> )	2.71 (3)			
Na...H—C(1 <sup>vlll</sup> )	3.21 (2)			
Na...H(1)—O(5 <sup>lll</sup> )	3.44 (3)			
Na...S <sup>lv</sup>	3.494 (1)			
Other contacts for 4CN-K				
K...H(2)—O(4 <sup>l</sup> )	3.04 (6) Å			
K...H(1)—O(4 <sup>lll</sup> )	3.23 (4)			
K...H—C(1 <sup>lv</sup> )	3.26 (3)			
K...H(1)—O(4 <sup>l</sup> )	3.34 (4)			
K...H(2)—O(4 <sup>lll</sup> )	3.36 (6)			
C(1)—H...O(1 <sup>v</sup> )	3.07 (4)			
O(4)...O(2 <sup>lv</sup> )	2.924 (2)			
C(1)...H(2)—O(4 <sup>ll</sup> )	2.64 (2)			
C(2)...O(3 <sup>ll</sup> )	3.178 (2)			
N(1)...O(4 <sup>vll</sup> )	3.023 (2)			
N(2)...O(3 <sup>l</sup> )	2.814 (2)			
N(3)...H—C(1 <sup>lv</sup> )	2.49 (4)			

### Symmetry operations

	4CN-NA	4CN-K
(i)	1 - x, -y, -z	1 - x, 1 - y, 2 - z
(ii)	x, y, -1 + z	1 - x, 1 - y, 1 - z
(iii)	-x, -y, 1 - z	2 - x, 1 - y, 1 - z
(iv)	-1 + x, y, z	1 + x, y, z
(v)	1 - x, 1 - y, 1 - z	x, y, -1 + z
(vi)	1 - x, -y, 1 - z	1 + x, y, -1 + z
(vii)	x, y, 1 + z	1 - x, -y, 1 - z
(viii)	-1 + x, y, 1 + z	

\* Doubtful bifurcated hydrogen bond.

The water molecules, two crystallographically independent in 4CN-NA and one in 4CN-K, form part of the coordination spheres of the cations and are involved in the hydrogen-bond schemes (Figs. 1 and 2). Both structures contain dimeric thiadiazine molecules formed through two centrosymmetric N(2)—H...O(3) intermolecular hydrogen bonds. Table 3 shows the geometrical features of the intermolecular contacts for both 4CN-NA and 4CN-K.

Tables 4 and 5 show a comparison of the bond lengths and bond angles respectively, for 4CN-NA and 4CN-K. Although there are several significant differences among the magnitudes of the bond lengths within the molecular rings of both compounds, one can assume a general similarity which is supported by a half-normal probability plot (Abrahams & Keve, 1971) calculated with these distances. This comparison, excluding the S—N(1) distance, gives a linear array with slope 1.7 (2), zero intercept at -0.1 (1) and a correlation coefficient of the fit of 0.96.

Table 4. Bond lengths (Å) with e.s.d.'s in parentheses

See Table 3 for symmetry operations.

	4CN-NA	4CN-K
S—O(1)	1.439 (1)	1.436 (2)
S—O(2)	1.435 (1)	1.435 (2)
S—N(1)	1.581 (1)	1.593 (1)
S—N(2)	1.651 (1)	1.650 (1)
N(1)—C(1)	1.324 (2)	1.329 (2)
N(2)—C(3)	1.374 (1)	1.372 (2)
N(2)—H	0.86 (2)	0.83 (2)
N(3)—C(4)	1.148 (2)	1.151 (2)
C(1)—C(2)	1.380 (1)	1.382 (2)
C(1)—H	0.92 (2)	0.96 (3)
C(2)—C(3)	1.431 (1)	1.436 (2)
C(2)—C(4)	1.421 (2)	1.419 (2)
C(3)—O(3)	1.241 (1)	1.241 (1)
O(4)—H(1)	0.87 (3)	0.84 (4)
O(4)—H(2)	0.86 (4)	0.94 (6)
O(5)—H(1)	0.82 (3)	
O(5)—H(2)	0.79 (3)	

	4CN-NA		4CN-K
Na—O(5)	2.353 (1)	K—O(4 <sup>iii</sup> )	2.752 (1)
Na—O(4)	2.386 (1)	K—O(4 <sup>v</sup> )	2.810 (2)
Na—O(2 <sup>v</sup> )	2.449 (1)	K—O(2 <sup>iv</sup> )	2.830 (2)
Na—N(3)	2.467 (1)	K—O(1 <sup>vii</sup> )	2.889 (1)
Na—O(1 <sup>vi</sup> )	2.501 (1)	K—O(1 <sup>vi</sup> )	2.903 (2)
Na—O(1 <sup>iv</sup> )	2.537 (1)	K—N(3)	2.916 (2)
		K—O(2 <sup>ii</sup> )	2.934 (2)

The observed bond lengths within the molecular ring of each compound can be explained in terms of some non-integer bond orders. This situation is common for most thiadiazine compounds (Esteban-Calderón *et al.*, 1982*b*, and literature cited therein). From the electron delocalization observed within the thiadiazine rings and from the mentioned similarity, we propose the common major electron distributions given in Fig. 3 according to Linnett's (1966) model. By comparing this electron-distribution model with the one proposed for the free heterocycle 4CN (Esteban-Calderón *et al.*, 1979), strong electron modifications are observed within the thiadiazine ring when Na<sup>+</sup> or K<sup>+</sup> ions are attached to it. Identical modifications in the bond lengths were found between 4NO<sub>2</sub> (Esteban-Calderón *et al.*, 1982*a*) and its sodium or potassium salts 4NO<sub>2</sub>-NA, 4NO<sub>2</sub>-K (Esteban-Calderón *et al.*, 1982*b*), the main modifications being around O(3), C(3), N(2), S and N(1). The same proton migration occurs in the syntheses of 4CN-NA and 4CN-K from 4CN, as reported for 4NO<sub>2</sub>-NA and 4NO<sub>2</sub>-K synthesized from 4NO<sub>2</sub>, in good agreement with the regioselective N(2) alkylation of 4CN and 4NO<sub>2</sub> performed in sodium or potassium hydroxide (Goya, Martínez, Ochoa & Stud, 1981).

Table 6 shows a comparison of several torsion angles for 4CN-NA and 4CN-K. Both thiadiazine rings can be described as 2,3-diplanar envelopes according to a conformational model for a six-membered ring (Cano, Foces-Foces & García-Blanco, 1977), the S

Table 5. Bond angles (°) with e.s.d.'s in parentheses

See Table 3 for symmetry operations.

	4CN-NA	4CN-K
O(1)—S—O(2)	113.1 (1)	114.7 (1)
O(1)—S—N(1)	110.4 (1)	110.7 (1)
O(1)—S—N(2)	108.5 (1)	106.9 (1)
O(2)—S—N(1)	110.3 (1)	109.8 (1)
O(2)—S—N(2)	108.1 (1)	108.9 (1)
N(1)—S—N(2)	106.2 (1)	105.4 (1)
S—N(1)—C(1)	121.7 (1)	118.2 (1)
S—N(2)—C(3)	126.2 (1)	123.7 (1)
S—N(2)—H	119 (2)	116 (2)
C(3)—N(2)—H	114 (2)	118 (2)
N(1)—C(1)—C(2)	126.9 (1)	127.2 (1)
N(1)—C(1)—H	114 (2)	115 (2)
C(2)—C(1)—H	119 (2)	118 (2)
C(1)—C(2)—C(3)	122.0 (1)	121.6 (1)
C(1)—C(2)—C(4)	120.9 (1)	120.9 (1)
C(3)—C(2)—C(4)	117.1 (1)	117.2 (1)
N(2)—C(3)—C(2)	116.7 (1)	116.2 (1)
N(2)—C(3)—O(3)	119.1 (1)	119.8 (1)
C(2)—C(3)—O(3)	124.2 (1)	123.9 (1)
C(2)—C(4)—N(3)	177.7 (1)	178.1 (1)
H(1)—O(4)—H(2)	102 (3)	99 (5)
H(1)—O(5)—H(2)	107 (3)	—

	4CN-NA		4CN-K
O(4)—Na—N(3)	84.97 (4)	O(2 <sup>iv</sup> )—K—N(3)	119.71 (5)
O(4)—Na—O(1 <sup>vi</sup> )	81.93 (4)	O(2 <sup>iv</sup> )—K—O(4 <sup>iii</sup> )	73.50 (5)
O(4)—Na—O(5)	159.62 (4)	O(2 <sup>iv</sup> )—K—O(4 <sup>v</sup> )	154.03 (4)
O(4)—Na—O(2 <sup>v</sup> )	112.24 (5)	O(2 <sup>iv</sup> )—K—O(1 <sup>vi</sup> )	97.32 (4)
O(4)—Na—O(1 <sup>iv</sup> )	81.95 (3)	O(2 <sup>iv</sup> )—K—O(2 <sup>ii</sup> )	87.81 (4)
N(3)—Na—O(1 <sup>vi</sup> )	93.84 (4)	O(2 <sup>iv</sup> )—K—O(1 <sup>vii</sup> )	93.46 (4)
N(3)—Na—O(5)	106.70 (4)	N(3)—K—O(4 <sup>iii</sup> )	133.51 (5)
N(3)—Na—O(2 <sup>v</sup> )	82.36 (4)	N(3)—K—O(4 <sup>v</sup> )	77.97 (5)
N(3)—Na—O(1 <sup>iv</sup> )	166.03 (5)	N(3)—K—O(1 <sup>vi</sup> )	133.30 (4)
O(1 <sup>vi</sup> )—Na—O(5)	80.68 (4)	N(3)—K—O(2 <sup>ii</sup> )	73.81 (5)
O(1 <sup>vi</sup> )—Na—O(2 <sup>v</sup> )	164.78 (4)	N(3)—K—O(1 <sup>vii</sup> )	75.21 (5)
O(1 <sup>vi</sup> )—Na—O(1 <sup>iv</sup> )	89.18 (3)	O(4 <sup>iii</sup> )—K—O(4 <sup>v</sup> )	80.55 (5)
O(5)—Na—O(2 <sup>v</sup> )	86.28 (4)	O(4 <sup>iii</sup> )—K—O(1 <sup>vi</sup> )	81.17 (4)
O(5)—Na—O(1 <sup>iv</sup> )	87.24 (4)	O(4 <sup>iii</sup> )—K—O(2 <sup>ii</sup> )	61.80 (4)
O(2 <sup>v</sup> )—Na—O(1 <sup>iv</sup> )	98.05 (4)	O(4 <sup>iii</sup> )—K—O(1 <sup>vii</sup> )	151.27 (4)
		O(4 <sup>v</sup> )—K—O(1 <sup>vi</sup> )	78.50 (5)
		O(4 <sup>v</sup> )—K—O(2 <sup>ii</sup> )	78.85 (5)
		O(1 <sup>vi</sup> )—K—O(2 <sup>ii</sup> )	139.51 (4)
		O(1 <sup>vi</sup> )—K—O(1 <sup>vii</sup> )	75.14 (4)
		O(2 <sup>ii</sup> )—K—O(1 <sup>vii</sup> )	144.89 (4)
		O(1 <sup>vii</sup> )—K—O(4 <sup>v</sup> )	110.28 (4)

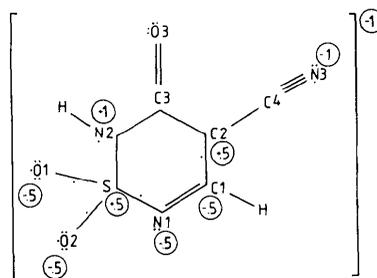


Fig. 3. Major electron distribution common for 4CN-NA and 4CN-K.

Table 6. *Torsion angles* ( $^\circ$ ) *with e.s.d.'s in parentheses*

	4CN-NA	4CN-K
N(2)–S–N(1)–C(1)	6.2 (2)	27.4 (2)
S–N(1)–C(1)–C(2)	–3.5 (2)	–13.1 (3)
N(1)–C(1)–C(2)–C(3)	–0.8 (2)	–6.0 (3)
C(1)–C(2)–C(3)–N(2)	0.8 (1)	4.3 (2)
C(2)–C(3)–N(2)–S	3.4 (2)	16.0 (2)
C(3)–N(2)–S–N(1)	–6.5 (1)	–30.4 (2)
C(3)–C(2)–C(4)–N(3)	16.0 (4)	–12.0 (6)
O(3)–C(3)–N(2)–S	–177.0 (1)	–167.3 (2)
O(3)–C(3)–C(2)–C(4)	1.7 (2)	1.3 (3)
O(1)–S–N(1)–C(1)	–111.2 (1)	142.6 (2)
C(3)–N(2)–S–O(2)	–124.9 (1)	87.3 (2)
O(2)–S–N(1)–C(1)	123.1 (1)	–89.8 (2)
O(1)–S–N(2)–C(3)	112.1 (1)	–148.3 (2)

Table 7. *Atomic deviations* ( $\text{\AA}$ ) *from least-squares planes* (Nardelli, Musatti, Domiano & Andreotti, 1965) *with e.s.d.'s in parentheses*

Atoms marked with asterisks are not included in the calculations.

Plane 1	4CN-NA	4CN-K
C(1)	0.003 (2)	0.024 (2)
C(2)	–0.004 (2)	–0.021 (2)
C(3)	0.003 (1)	0.013 (2)
N(1)	0.000 (2)	–0.009 (2)
N(2)	–0.001 (1)	–0.002 (2)
*S	–0.092 (1)	–0.429 (1)
*C(4)	–0.030 (2)	0.039 (2)
*N(3)	–0.064 (2)	0.097 (2)
*O(3)	0.017 (1)	0.112 (2)
Plane 2	4CN-NA	4CN-K
O(3)	0.005 (1)	0.003 (2)
C(3)	–0.010 (1)	–0.006 (2)
C(2)	0.007 (1)	0.004 (2)
C(4)	0.005 (2)	–0.002 (2)
N(3)	–0.010 (2)	–0.000 (2)
*O(4)	0.543 (1)	–1.490 (2)
*Na	0.542 (1)	–
*K	–	0.716 (1)
Plane 3	4CN-NA	4CN-K
S	0.000 (1)	0.000 (1)
O(1)	0.000 (1)	0.000 (2)
O(2)	0.000 (1)	0.000 (2)
Angles between planes	4CN-NA	4CN-K
1/2	1.1 (4) $^\circ$	4.3 (4) $^\circ$
1/3	90.0 (4)	90.0 (4)
2/3	89.4 (4)	93.4 (4)

atom being at the flap. Table 7 gives the atomic deviations from several molecular planes.

Each  $Na^+$  ion in 4CN-NA is surrounded by three O atoms of type O(1) and O(3), one N(3) atom of the cyano group, and two water molecules, O(4) and O(5), forming a somewhat distorted octahedron (Fig. 1, Tables 4 and 5). The  $Na^+$  ion still seems to interact with

the O(3) atom of the bidentate ligand through a water molecule O(4), forming a non-planar seven-membered ring, the  $Na^+$  ion and the O(4) atom being 0.542 and 0.543  $\text{\AA}$  out of the plane respectively (Table 7, plane 2). Similar situations of indirect cation–anion interactions have been reported in the structures of several barium compounds (Shefter & Trueblood, 1965; Furberg & Mostad, 1962).

The  $K^+$  ions in 4CN-K show a coordination number of seven. Four O atoms of type O(1) and O(2), one N(3) atom of the cyano group, and two equivalent water molecules, O(4), form a pentagonal bipyramid around  $K^+$  (Fig. 2). As occurs with  $Na^+$  in the case of 4CN-NA,  $K^+$  interacts indirectly with the O(3) atom of the bidentate ligand through a water molecule, O(4). However, in this case, the  $K^+ \cdots O(4) \cdots O(3)$  and  $K^+ \cdots N(3)$  interactions occur with different thiazidine molecules (Fig. 2), so that no seven-membered ring is formed as occurs in 4CN-NA (Fig. 1).

The preference of the higher-charge-density cation ( $Na^+$ ) for an anionic environment observed in 4NO<sub>2</sub>-NA *vs*  $K^+$  in 4NO<sub>2</sub>-K (Esteban-Calderón *et al.*, 1982*b*) is also shown in 4CN-NA and 4CN-K. In fact, excluding the indirect interaction with O(3) through the water molecule,  $Na^+$  makes contact with four anionic sites (Fig. 1), whereas  $K^+$  is bonded to five anionic sites, supporting the general rule that the intensity of the cation–anion interaction increases with the charge density of the cation (Poonia & Bajaj, 1979). This can also be evaluated in terms of the observed Na–O, –N and K–O, –N bond lengths, as was done in 4NO<sub>2</sub>-NA and 4NO<sub>2</sub>-K. On the basis of ionic and van der Waals radii, one can obtain the expected distances given in the caption to Fig. 4. The average cation–neighbour distances observed in the sodium salts 4NO<sub>2</sub>-NA and 4CN-NA are only 1.1 and 1.5% respectively, elongated with respect to the expected ones. In the potassium salts 4NO<sub>2</sub>-K and 4CN-K, these deviations are much greater (dashed line in Fig. 4) and agree with the changeability of  $K^+$  *vs* the retention suffered by  $Na^+$ . However, excluding the water molecules, *i.e.* taking into account the distances between cation and anion sites only, a clear difference is observed between both sodium compounds 4NO<sub>2</sub>-NA and 4CN-NA (full line in Fig. 4), which may indicate a cationic exchangeability for 4CN-NA somewhat greater than for 4NO<sub>2</sub>-NA. This different behaviour expected for 4CN-NA *vs* 4NO<sub>2</sub>-NA is indirectly observed. In fact, methylation of 4NO<sub>2</sub> performed in sodium bicarbonate afforded only the N(2)-methyl derivative, whereas methylation of 4CN in the same medium also gives an O(3), N(1)-dimethyl derivative as a minor component (Goya *et al.*, 1981). The formation of this dimethyl derivative can be explained assuming a lower tendency of 4CN to form strong chelates with  $Na^+$ , and this could probably be understood in terms of the different arrangement of  $Na^+$ -bidentate ligand observed in

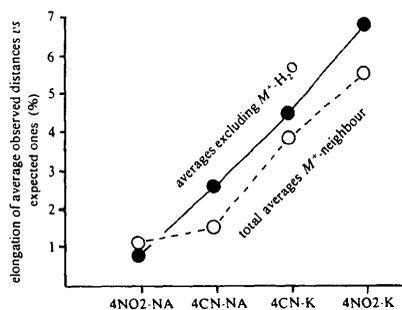


Fig. 4. Cation-dipole interaction model; ionic and van der Waals radii: Na<sup>+</sup> 0.97, K<sup>+</sup> 1.33 (*Handbook of Chemistry and Physics*, 1977), O 1.40, N 1.50 Å (Bondi, 1964); expected distances: Na<sup>+</sup>-O 2.37, Na<sup>+</sup>-N 2.47, K<sup>+</sup>-O 2.73, K<sup>+</sup>-N 2.83 Å.

4CN-NA and 4NO<sub>2</sub>-NA. In 4NO<sub>2</sub>-NA, Na<sup>+</sup> makes contact directly with the bidentate ligand, whereas in 4CN-NA this interaction is, in part, indirect through a water molecule (Fig. 1).

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### *trans*-Bis(2-aminoethanol)diodoplatinum(II)

BY F. D. ROCHON AND R. MELANSON

*Département de Chimie, Université du Québec à Montréal, CP 8888, Montréal, Canada H3C 3P8*

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#### Abstract

*trans*-[Pt(NH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-OH)<sub>2</sub>I<sub>2</sub>], C<sub>4</sub>H<sub>14</sub>I<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Pt, *M<sub>r</sub>* = 571.07, was synthesized from the isomerization of the *cis* compound in water. It crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c* with *a* = 9.838 (5), *b* = 14.919 (6), *c* = 8.351 (3) Å, β = 96.76 (4)°, *V* = 1217 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 3.116, *D<sub>m</sub>* = 3.12 (1) Mg m<sup>-3</sup> (floatation) and μ(Mo Kα) = 16.637 mm<sup>-1</sup>. The parameters were refined by full-matrix least-squares calculations to a conventional *R* of 0.057 and *R<sub>w</sub>* = 0.056 for 1590 observed reflections. The coordination

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#### References

- ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* **A27**, 157-165.
- BONDI, A. (1964). *J. Phys. Chem.* **68**, 441-451.
- CANO, F. H., FOCES-FOCES, C. & GARCÍA-BLANCO, S. (1977). *Tetrahedron*, **33**, 797-802.
- ESTEBAN-CALDERÓN, C., MARTÍNEZ-RIPOLL, M. & GARCÍA-BLANCO, S. (1979). *Acta Cryst.* **B35**, 2795-2797.
- ESTEBAN-CALDERÓN, C., MARTÍNEZ-RIPOLL, M. & GARCÍA-BLANCO, S. (1982*a*). *Acta Cryst.* **B38**, 1340-1342.
- ESTEBAN-CALDERÓN, C., MARTÍNEZ-RIPOLL, M. & GARCÍA-BLANCO, S. (1982*b*). *Acta Cryst.* **B38**, 1124-1128.
- FURBERG, S. & MOSTAD, A. (1962). *Acta Chem. Scand.* **16**, 1627-1636.
- GOYA, P., MARTÍNEZ, P., OCHOA, C. & STUD, M. (1981). *J. Heterocycl. Chem.* In the press.
- GOYA, P. & STUD, M. (1978). *J. Heterocycl. Chem.* **15**, 253-256.
- Handbook of Chemistry and Physics* (1977). 57th ed., p. F-213. Ohio: CRC Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- LINNETT, J. W. (1966). *The Electronic Structure of Molecules. A New Approach*. London: Methuen.
- NARDELLI, M., MUSATTI, A., DOMIANO, P. & ANDRETTI, G. (1965). *Ric. Sci.* **35**, 807-810.
- POONIA, S. N. & BAJAJ, V. A. (1979). *Chem. Rev.* **79**, 389-445.
- SHEFTER, E. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* **18**, 1067-1077.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland

around the Pt atom is square-planar. The Pt-I bond distances are 2.604 (1) and 2.602 (1) Å, while the Pt-N bonds are 2.047 (15) and 2.082 (13) Å. The crystal is stabilized by intermolecular hydrogen bonds between the hydroxyl groups.

#### Introduction

Since the discovery of the antitumor activity of some Pt compounds, the importance of Pt chemistry has markedly increased. We have been involved, for many

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