Allen, F. H., Davies, J. E., Galloy, J. J., Johnson, O., Kennard, O., Macrae, C. F., Mitchell, G. F., Smith, J. M. & Watson, D. G. (1991). *J. Chem. Inf. Comput. Sci.* **31**, 187–204.
Breuer, S. W. & Small, R. W. H. (1983). *Eur. Crystallogr. Meet.* **8**, 190.
Breuer, S. W. & Small, R. W. H. (1991). *Acta Cryst.* C**47**, 871–872.
Canty, A. J., Chaichet, N. & Gatehouse, B. M. (1980). *Acta Cryst.* B**36**, 786–789.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
Davies, K. (1983). *SNOOPI. Program for Drawing Crystal and Molecular Diagrams.* Univ. of Oxford, England.
Drew, M. G. B., McFall, S. G. & Nelson, S. M. (1979). *J. Chem. Soc. Dalton Trans.* pp. 575–581.
Gleghorn, J. T. & Small, R. W. H. (1995). *Acta Cryst.* B**51**. 346–353.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.
Small, R. W. H. (1977). *DATR. Program for Reducing Raw Stadi-2 Data to Intensities.* Univ. of Lancaster, England.

Acta Cryst. (1995). C**51**, 1788–1791

Bis(2,4-dinitrophenolato)(triethanolamine)-calcium(II)

Geeta Hundal (née Sood) and Martin Martínez-Ripoll

Departmento de Cristalografía, Instituto de Química-Física Rocasolano, CSIC, Serrano 119, E-28006 Madrid, Spain

Maninder Singh Hundal

Department of Chemistry, Guru Nanak Dev University, Amritsar 143005, India

Narinder Singh Poonia

Department of Chemistry, Devi Ahilya University, Indore, India

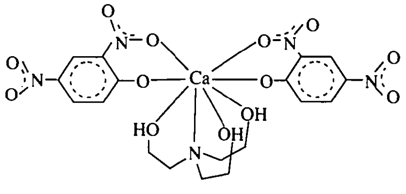
(*Received* 3 *January* 1995; *accepted* 14 *March* 1995)

Abstract

The title complex, bis(2,4-dinitrophenolato-O,O^2)-(2,2′,2″-nitrilotriethanol-N,O,O',O'')calcium(II), $[Ca(C_6H_3N_2O_5)_2(C_6H_{15}NO_3)]$, is monomeric and the Ca^{2+} ion is eight-coordinate. Both dinitrophenolate ligands coordinate to the metal ion by their phenolic O atoms and one O atom of the *ortho*-nitro group. Ca is further coordinated by all the O atoms and the N atom of triethanolamine, the O atoms of which are also hydrogen-bond donors. The phenolic O atoms and one O atom of a *para*-nitro group take part in intermolecular hydrogen bonding.

Comment

Chemical and X-ray structural studies on systems of the type M^{z+}(anions)(ligand)(H_2O), where M^{z+} is an alkali or alkaline earth cation, the anions are picrate, *o*-nitrophenolate, 3,5-dinitrobenzoate and 2,4-dinitrophenolate (dnp), and the ligands are triethanolamine (tea), diethanolamine (dea), 1,10-phenanthroline, tetraethylene gylcol (teg) and triethylene glycol (treg), have revealed that the metal–ligand interaction is more affected by the nature of the counter anion than is known in the case of transition metal cations (Bajaj & Poonia, 1988). It has also been found that the hydrogen bonding of the anion in the system aids the complexation of the *s*-block metal ions. This led us to investigate ligands such as ethanolamines which can coordinate with the cation and stabilize the anion at the same time. The X-ray structural results for Ba(picrate)$_2$(tea)$_2$ and Ba(dnp)$_2$(tea)$_2$ have been reported (Kanters, de Koster, Schouten, Venkatasubramanian & Poonia, 1985; Kanters, Smeets, Venkatasubramanian & Poonia, 1984); those of the title compound, (I), are presented here as part of our investigation of the discrimination among Ca^{2+}, Sr^{2+} and Ba^{2+} ions in Group II.



(I)

An *ORTEP* (Johnson, 1965) diagram of the molecule is shown in Fig. 1. Ca is eightfold coordinated by the two dnp molecules and one tea molecule. Both dnp anions are coordinated through their phenolic O atoms and one of the O atoms of the *o*-nitro groups. The tea ligand coordinates using all four potential donor atoms, *i.e.* three O atoms and one N atom. The important bond distances, angles and torsion angles are given in Table 2. The Ca—O distances are in the range 2.343 (5)–2.547 (7) Å and the Ca—N distance is 2.600 (7) Å. The coordination polyhedron of Ca can be classified as a distorted square antiprism.

Corresponding bond lengths in the two dnp ligands do not show significant differences, the largest being 0.028 Å for the N—O bonds. The C—O bond lengths of 1.279 (9) and 1.283 (8) Å are comparable to those of 1.273 (5) and 1.283 (6) Å found in the Ba complex (Kanters *et al.*, 1984). In both dnp residues, the two C—C bonds at the phenolic site are long [average 1.430 (11) Å] and two out of the remaining bonds are short [average 1.362 (12) Å], whereas the bond angles at the phenolic site are smaller than 120°

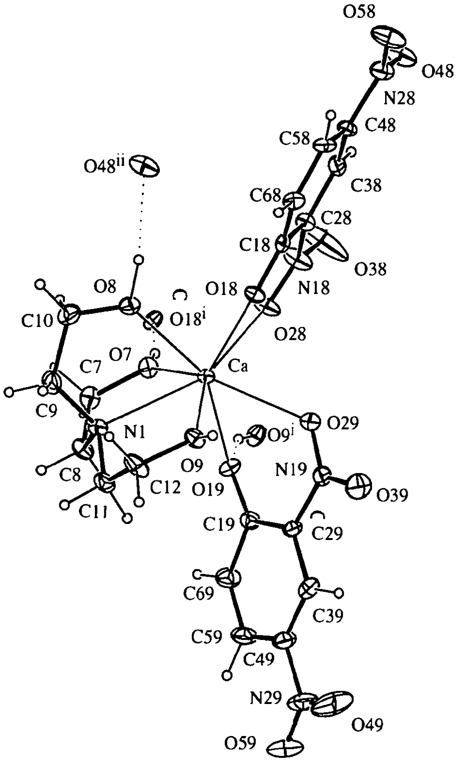


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the final X-ray model showing the atomic labelling and the hydrogen-bonding scheme. The non-H atoms are shown with displacement ellipsoids drawn at the 30% probability level. H-atom labels have been omitted for clarity. Symmetry codes: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $-x, 1 - y, -z$.

[average 114.6 (6)°]. These differences are consistent with the contributions of quinonoid resonance structures to the molecular structure (Bush & Truter, 1971) and second-order hybridization at the ring C atoms bearing neighbouring substituents (Hughes, 1973). The *o*-nitro group of dnp8 (see Table 1 and Fig. 1) is rotated by 5.2 (5)° with respect to the plane of the aromatic ring; the rotation angle of the *p*-nitro group is 1.8 (7)°. For dnp9 these values are 1.9 (6) and 7.9 (6)°, respectively. Hence, both dnp anions exhibit a twisting of the *o*-nitro group with respect to the plane of the aromatic ring, which is a common feature in *o*-nitrophenolates and should be considered as a consequence of molecular overcrowding (Krogh Andersen & Krogh Andersen, 1975). However, this twisting has been found to be slightly greater in dnp8 than in dnp9, perhaps due to crystal packing.

As in the tea complexes of NaI, Sr(nitrate)$_2$ and Ba(acetate)$_2$ (Voegele, Fischer & Weiss, 1974*a*,*b*; Voegele, Thierry & Weiss, 1974), and the aforementioned Ba complex, the tea ligand here should be considered as having an extended conformation. This requires at least three nearly planar C—N—C—C fragments and a *gauche* conformation of the terminal OH groups with respect to the C—N bonds. The N—C—C—O torsion angles [44.5 (10)–56.2 (9)°, Table 2] are comparable to those [46.8 (4)–67.4 (4)°] reported in the literature (Voegele *et al.*, 1974; Kanters *et al.*, 1984), producing nearly *gauche* conformations of the terminal OH groups with respect to the C—N bonds. There are also three nearly planar C—N—C—C fragments with torsion angles ranging from 141.1 (8) to −166.8 (7)° (Table 2), which are comparable to the values found in the literature.

All three hydroxyl groups coordinate to Ca^{2+} and take part as donors in intermolecular hydrogen bonding. Both the phenolic atoms O18 and O19 are strong acceptors, forming hydrogen bonds with O7 and O9 of the tea molecule. O8 forms a weak hydrogen bond with one of the O atoms, O48, of the *p*-nitro group of dnp8 (Table 3).

The common feature of all these systems is extensive hydrogen bonding between the tea hydroxyl protons and the anionic O atoms of the dinitrophenolate, in addition to those formed with the nitro O atoms. The present structure completes the series M(dnp)$_2$(tea)$_x$ (where x = 1 or 2 and M = Ca^{2+}, Sr^{2+} or Ba^{2+}). The structure of Sr(dnp)$_2$(tea)$_2$ is to be published elsewhere (Poonia, Sheldrick & Hundal, 1995). In the case of Sr(dnp)$_2$(tea)$_2$, the cation is not coordinated to the anion at all (the nearest phenolate group is at a distance of 4.27 Å), whereas in Ba(dnp)$_2$(tea)$_2$ the cation is sandwiched between two tea ligands and the dnp ligand has only one contact with the metal ion through the O atom of the nitro group (Ba—O 2.785 Å). In the title compound, Ca is coordinated to both dnp anions. The structure analysis of the entire series reveals that as one moves down the group, the amount of metal–counter anion interaction decreases.

Experimental

The compound was synthesized by 1:1 reaction between calcium(2,4-dinitrophenolate)$_2$ and triethanolamine in aqueous ethanol. The crystals were grown at room temperature by slow evaporation. The density D_m was measured by flotation in water/KI.

Crystal data

[Ca(C$_6$H$_3$N$_2$O$_5$)$_2$-(C$_6$H$_{15}$NO$_3$)]
$M_r = 555.47$
Monoclinic
$P2_1/c$
$a = 22.935\ (3)$ Å
$b = 8.746\ (1)$ Å
$c = 11.702\ (1)$ Å
$\beta = 95.66\ (1)°$
$V = 2335.9\ (4)$ Å^3
$Z = 4$
$D_x = 1.579$ Mg m^{-3}
$D_m = 1.582$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 38 reflections
$\theta = 5$–$15°$
$\mu = 0.335$ mm^{-1}
$T = 298$ K
Prism
0.3 × 0.2 × 0.1 mm
Orange

Data collection

Philips PW1100 diffractometer
ω scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.83$, $T_{\max} = 1.00$
4605 measured reflections
4099 independent reflections

2122 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.019$
$\theta_{\max} = 25°$
$h = -28 \rightarrow 28$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 15$
2 standard reflections
frequency: 90 min
intensity decay: 1%

Refinement

Refinement on F
$R = 0.063$
$wR = 0.057$
$S = 1.178$
2122 reflections
334 parameters
H-atom parameters not refined
$w = K/(a + b|F_o|)^2$ (see below)

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.05$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$
Ca	0.2330 (1)	0.2269 (2)	0.0138 (1)	0.02803 (4)
O18	0.1671 (2)	0.3810 (6)	0.1106 (4)	0.036 (1)
O28	0.1766 (3)	0.4062 (7)	−0.1168 (5)	0.052 (2)
O38	0.1234 (5)	0.5691 (14)	−0.2084 (7)	0.185 (5)
O48	−0.0306 (3)	0.8381 (8)	−0.0713 (6)	0.072 (2)
O58	−0.0477 (3)	0.8140 (10)	0.1055 (6)	0.087 (2)
N18	0.1377 (3)	0.5019 (10)	−0.1206 (6)	0.062 (3)
N28	−0.0192 (3)	0.7852 (10)	0.0251 (7)	0.055 (2)
C18	0.1236 (3)	0.4709 (9)	0.0868 (6)	0.033 (2)
C28	0.1062 (3)	0.5360 (9)	−0.0222 (6)	0.035 (2)
C38	0.0594 (4)	0.6372 (9)	−0.0439 (7)	0.042 (2)
C48	0.0286 (3)	0.6763 (10)	0.0468 (7)	0.039 (2)
C58	0.0419 (3)	0.6136 (11)	0.1549 (7)	0.043 (2)
C68	0.0878 (3)	0.5156 (10)	0.1760 (6)	0.039 (2)
O19	0.3193 (2)	0.2486 (7)	−0.0768 (4)	0.042 (1)
O29	0.2923 (3)	0.4664 (7)	0.0694 (5)	0.053 (2)
O39	0.3611 (3)	0.5584 (8)	0.1886 (6)	0.072 (2)
O49	0.5563 (4)	0.4049 (15)	0.2033 (9)	0.141 (5)
O59	0.5872 (3)	0.2705 (12)	0.0679 (8)	0.125 (4)
N19	0.3447 (3)	0.4735 (8)	0.1081 (6)	0.043 (2)
N29	0.5485 (4)	0.3334 (14)	0.1161 (10)	0.087 (4)
C19	0.3717 (3)	0.2771 (10)	−0.0331 (6)	0.040 (2)
C29	0.3875 (3)	0.3784 (10)	0.0584 (7)	0.040 (2)
C39	0.4456 (4)	0.3948 (11)	0.1071 (7)	0.050 (2)
C49	0.4882 (4)	0.3126 (12)	0.0618 (9)	0.058 (3)
C59	0.4763 (4)	0.2154 (13)	−0.0315 (9)	0.066 (3)
C69	0.4203 (4)	0.1990 (12)	−0.0781 (8)	0.059 (3)
O7	0.2130 (2)	0.0884 (6)	−0.1666 (4)	0.039 (1)
O8	0.1568 (2)	0.0687 (7)	0.0715 (5)	0.053 (2)
O9	0.2908 (2)	0.1738 (6)	0.1936 (4)	0.043 (2)
N1	0.2631 (3)	−0.0595 (8)	0.0297 (5)	0.037 (2)
C7	0.2314 (4)	−0.0673 (10)	−0.1792 (7)	0.045 (2)
C8	0.2787 (4)	−0.1055 (10)	−0.0860 (7)	0.044 (2)
C9	0.2148 (4)	−0.1543 (10)	0.0674 (8)	0.054 (3)
C10	0.1549 (4)	−0.0840 (12)	0.0423 (8)	0.060 (3)
C11	0.3158 (4)	−0.0656 (11)	0.1144 (8)	0.054 (2)
C12	0.3070 (4)	0.0194 (11)	0.2216 (8)	0.059 (3)

Table 2. *Selected geometric parameters* (Å, °)

Ca—O18	2.392 (5)	Ca—O28	2.465 (6)
Ca—O19	2.343 (5)	Ca—O29	2.547 (7)
Ca—O7	2.438 (5)	Ca—O8	2.379 (6)
Ca—O9	2.419 (5)	Ca—N1	2.600 (7)
O18—Ca—O28	67.5 (2)	O18—Ca—O19	140.4 (2)
O18—Ca—O29	76.2 (2)	O18—Ca—O7	128.1 (2)
O18—Ca—O8	71.2 (2)	O18—Ca—O9	90.8 (2)
O18—Ca—N1	133.2 (2)	O28—Ca—O19	94.8 (2)
O28—Ca—O29	82.5 (2)	O28—Ca—O7	74.7 (2)
O28—Ca—O8	101.0 (2)	O28—Ca—O9	150.5 (2)
O28—Ca—N1	140.9 (2)	O19—Ca—O29	66.1 (2)
O19—Ca—O7	75.2 (2)	O19—Ca—O8	148.5 (2)
O19—Ca—O9	89.7 (2)	O19—Ca—N1	83.1 (2)
O29—Ca—O7	132.9 (2)	O29—Ca—O8	142.6 (2)
O29—Ca—O9	72.7 (2)	O29—Ca—N1	130.0 (2)
O7—Ca—O8	82.9 (2)	O7—Ca—O9	134.3 (2)
O7—Ca—N1	67.0 (2)	O8—Ca—O9	89.8 (2)
O8—Ca—N1	67.5 (2)	O9—Ca—N1	68.5 (2)
O7—C7—C8—N1	48.6 (9)	C8—N1—C9—C10	−95.3 (9)
O8—C10—C9—N1	−44.5 (10)	C8—N1—C11—C12	163.9 (7)
O9—C12—C11—N1	−56.2 (9)	C9—N1—C11—C12	−71.5 (9)
C7—C8—N1—C9	68.9 (9)	C10—C9—N1—C11	141.1 (8)
C7—C8—N1—C11	−166.8 (7)		

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O7—H7···O18$^{\rm i}$	0.96	1.78	2.73 (1)	168
O8—H8···O48$^{\rm ii}$	1.12	2.02	3.00 (1)	145
O9—H9···O19$^{\rm iii}$	0.87	1.97	2.78 (1)	155

Symmetry codes: (i) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $-x, 1-y, -z$; (iii) $x, \frac{1}{2}-y, \frac{1}{2}+z$.

The structure was solved by the heavy-atom method. The position of the Ca atom was determined from a Patterson map and subsequent Fourier refinement revealed the rest of the structure. Refinement was carried out isotropically and then anisotropically. All H atoms were fixed geometrically except for three belonging to the hydroxyl groups, which were located in a difference Fourier map using data for which $\sin\theta/\lambda \leq 0.4$. Weights were applied according to $w = K/(a + b|F_o|)^2$ (*PESOS*; Martínez-Ripoll & Cano, 1975), where for $0 \leq F_o \leq 6.0$, $a = 1.48$ and $b = 0.19$, for $6.0 < F_o \leq 15.5$, $a = 3.37$ and $b = -0.12$, and for $15.5 < F_o$, $a = 0.97$ and $b = 0.04$.

Data collection: Philips PW1100 diffractometer software. Cell refinement: *LSUCRE* (Appleman, unpublished). Data reduction: *XRAY*80 (Stewart, 1980). Program used to solve structure: *DIRDIF* (Beurskens *et al.*, 1992). Program used to refine structure: *XRAY*80. Molecular graphics: *ORTEP* (Johnson, 1965) in *Xtal*3.2 (Hall, Flack & Stewart, 1994). Software used to prepare material for publication: *CSU* (Vicković, 1986).

GH is grateful to the Ministry of Science and Education in Spain for the award of a post doctoral fellowship.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving non-H atoms, and torsion angles have been deposited with the IUCr (Reference: NA1155). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bajaj, A. V. & Poonia, N. S. (1988). *Coord. Chem Rev.* **87**, 55–213.

Beurskens, P. T., Admiraal, G., Beurkens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, Univ. of Nijmegen, The Netherlands.

Bush, M. A. & Truter, M. R. (1971). *J. Chem. Soc. A*, pp. 745–750.

Hall, S. R., Flack, H. D. & Stewart, J. M. (1994). Editors. *Xtal3.2 Reference Manual*. Univs. of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.

Hughes, D. L. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2347–2354.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Kanters, J. A., de Koster, A., Schouten, A., Venkatasubramanian, K. & Poonia, N. S. (1985). *Acta Cryst.* C**41**, 1585–1588.

Kanters, J. A., Smeets, W. J. J., Venkatasubramanian, K. & Poonia, N. S. (1984). *Acta Cryst.* C**40**, 1701–1704.

Krogh Andersen, E. & Krogh Andersen, I. G. (1975). *Acta Cryst.* B**31**, 391–393.

Martínez-Ripoll, M. & Cano, F. H. (1975). *PESOS*. Instituto Rocasolano, CSIC, Serrano 119, E-28006 Madrid, Spain.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Poonia, N. S., Sheldrick, W. S. & Hundal, M. S. (1995). *J. Chem. Crystallogr.* Submitted.

Stewart, J. M. (1980). Editor. *The XRAY System of Crystallographic Programs*. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

Vicković, I. (1986). 10th Eur. Crystallogr. Meet., Wrocław, Poland. Abstract 3D-29.

Voegele, J. C., Fischer, J. & Weiss, R. (1974*a*). *Acta Cryst.* B**30**, 62–65.

Voegele, J. C., Fischer, J. & Weiss, R. (1974*b*). *Acta Cryst.* B**30**, 66–69.

Voegele, J. C., Thierry, J. C. & Weiss, R. (1974). *Acta Cryst.* B**30**, 70–75.

Acta Cryst. (1995). C**51**, 1791–1793

Dichlorobis(purine)zinc(II)

Heather L. Laity and Max R. Taylor*

The Flinders University of South Australia, School of Physical Sciences, GPO Box 2100, Adelaide, SA 5001, Australia

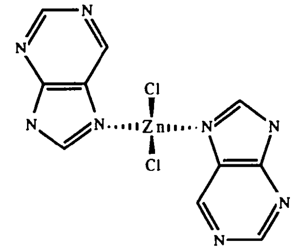
(*Received* 4 *August* 1994; *accepted* 23 *March* 1995)

Abstract

In the crystal structure of the title compound, [$ZnCl_2(C_5H_4N_4)_2$], the Zn atom is found to be tetrahedrally coordinated by two Cl atoms and N7 of each of the two purine ligands, with Zn—Cl 2.222 (1) and 2.229 (2) Å, and Zn—N7 2.027 (3) and 2.033 (4) Å.

Comment

The title compound, (I), was prepared and its structure determined during the course of our ongoing study of nucleobases and their analogues (*e.g.* Cunane & Taylor, 1993). The complex exhibits tetrahedral coordination geometry typical of Zn ions, with two Cl atoms and N7 of each of two purine molecules being the ligating atoms. Table 2 shows that, although the ligands are crystallographically distinct, there are no significant differences between those corresponding bond lengths and angles that are expected to be chemically equivalent. The Zn atom is similarly coordinated to N7 in trichloropuriniumzinc(II) (Sheldrick, 1982) and apart from differences near the protonation site (N1), the bond lengths and angles in the two structures are similar.



(I)

Molecules are linked along the polar *a* axis by intermolecular hydrogen bonds as shown in Fig. 2 [N1···N9′($x + \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$) 2.797 (6) and N1′··· N9($x - 1, y - 1, z - \frac{1}{2}$) 2.784 (5) Å].

This structure is one of a number of similar ones where the preferred coordination site of purine analogues to the Zn atom is N7. In solutions of purine,

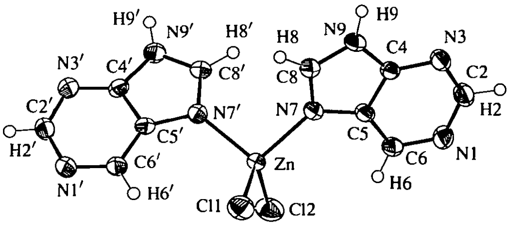


Fig. 1. A view of the molecule with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as circles of arbitrary radii.

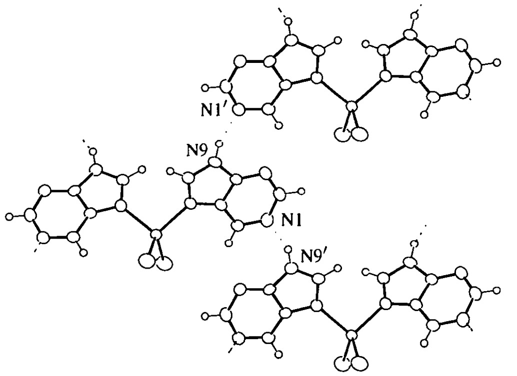


Fig. 2. A view of part of the structure showing hydrogen bonding.