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ORIGINAL PAPER

Synthesis and Crystal Structure of Bis (Tetrabutylammonium) (4,4′-Azodi(phenylcyanamide)) Salt · $[(n\text{-Bu})_4N]_2$ $[\text{Azodicyd}^{2-}]$ · H_2O

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Abstract The chemical preparation and crystal structure for a 4,4′-azodi(phenylcyanamide) salt) in the solid state are reported. This compound crystallizes in the triclinic space group $P\bar{1}$ with the following unit cell parameters: a = 9.759(3) Å, b = 11.237(4) Å, c = 11.919(4) Å, α = 95.54(3)°, β = 98.50(3)°, γ = 109.39(2)°, Z = 1 and V = 1204.4(7) Å^3. The 4,4′-azodi(phenylcyanamide) dianion, azodicyd^{2-}, is approximately planar, with the cyanamide groups (–N=C=N) in an *anti* conformation relative to each other and the azo group (–N=N–) adopting the more thermodynamically stable *trans* conformation. The crystal X-ray analysis shows that there are one azo molecule cation, two tetrabutylammonium cations and one water molecule in unit cell. Intermolecular O–H···N hydrogen bonds may be effective in the stabilization of the crystal structure of this compound and to form linear chain structure in the packing.

Keywords 4,4′-Azodi(phenylcyanamide) · Cyanamide groups · Hydrogen bond · Crystal structure

Introduction

Recently, phenylcyanamide ligand families are of considerable interest due to their importance as materials that possess useful optical, magnetic, and/or electronic properties. The phenyl cyanamide ligands are expected to be as potentially rich as that of the pseudohalids (for example, azide or thiocyanate). The attachment of a phenyl ring to the cyanamide group adds an extra dimension not present in azide or thiocyanate ligands [1–5]. The cyanamide group is a three-atom π-system in which the amine non-bonding electrons can delocalize into the nitrile π-bonds. Accordingly, the cyanamide group is expected to be a poorer π-acceptor but better donor than analogous nitrile ligand. For this reason, cyanamides are expected to be less sensitive to base hydrolysis. The phenylcyanamide ligand families have been used in architecture of hybrid polymeric materials and mixed-valance complexes because of its abilities in forming bridge via cyanamide groups [6, 7]. Here, we report the synthesis and X-ray determination of a 4,4′-azodiphenylcyanamide salt (azodicyd^{2-}).

Experimental

All chemicals were of analytical reagent grade and were used directly without further purification. Elemental analysis (C, H, N) was performed with a Perkin-Elmer 2400 CHN/O elemental analyzer. IR spectra (4000–400 cm^{-1}) were measured on a FT-IR JASCO 460 spectrophotometer with KBr pellets. Electronic spectra were recorded using a CARY 100 Bio VARIAN UV–Vis spectrophotometer. ^{1}H NMR spectrum was recorded on a Bruker FT-NMR 500 (500 MHz) Ultra Shield spectrometer at ambient temperature in DMSO-d$_6$.

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Synthesis of $[(n\text{-Bu})_4\text{N}]_2[\text{azodicyd}] \cdot 2\text{H}_2\text{O}$

Ammonium thiocyanate (1.5 g, 20 mmol) was dissolved in 20 mL of acetone and brought to a boil. To this was added dropwise a solution of benzoyl chloride (2.8 g, 20 mmol) in 20 mL of acetone, and the mixture was refluxed for an additional 15 min. 4,4′-Azodianiline (2.1 g, 9.9 mmol) was dissolved in 150 mL of boiling acetone and then slowly added to the refluxing mixture above. The mixture was refluxed for 1 h and then poured into a beaker containing 800 mL of water. The brown benzoyl thiourea precipitate was removed by suction filtration and dissolved in 300 mL of boiling 2 M NaOH. The resulting deep red solution was boiled for 5 min and then cooled to 60 °C. Lead acetate (7.5 g, 20 mmol) was dissolved in 20 mL of water and added to the thiourea solution. The temperature was maintained at 60 °C for 15 min, forming a black PbS precipitate, and the mixture was then filtered by suction into an ice-cooled flask. The filtrate was acidified to pH 5 with the addition of 25 g of glacial acetic acid, and a green precipitate were removed by suction filtration. Recrystallization from 700 mL of boiling acetone afforded a greenish gold solid. (This greenish gold solid was azodicydH_2). A (0.098 g, 0.37 mmol) azodicydH_2 was dissolved in 100 mL of boiling 2/1 acetone/water solution and was added excess triethylamine. To this was added a solution of $[\text{N}(n\text{-But})_4]\text{Cl}$ (0.194 g, 0.80 mmol) in 20 mL of water, and the mixture was stirred and heated for 15 min. The red precipitate was collected and washed with 30 mL of water. Single crystal suitable for X-ray diffraction was grown by slow diffusion of diethyl ether in to an acetone solution at 298 K. Anal. Calcd for C46H82N8O1: C, 72.44; H, 10.76; N, 14.70%. Found: C, 72.40; H, 10.69; N, 14.75%. IR (KBr):3058 (m), 3408 (m), 2960 (m), 2872 (m), 2093 (s), 1578 (s), 1543 (m), 1491 (s), 1341 (s), 1235 (m), 1134 (s), 876 (m), 842 (m), 740 (m) cm^{-1}. ^{1}H NMR (500 MHz): 7.42 (4H, d), 6.62 (4H, d), 3.13(16H, t), 1.54 (16H, q), 1.30 (16H, m), 0.9 (24H, t) ppm.

X-ray Crystallography

A red single crystal with dimension of 0.45 mm × 0.15 mm × 0.1 mm was chosen for X-ray diffraction study. Diffraction measurements were carried out on a STOE IPDS II two-circle diffractometer using graphite-monochromated Mo-K_α ($\lambda = 0.71073$ Å) radiation at 173 K. Cell parameters were determined by the least-squares calculation with θ angle ranging from 1.75 to 25.60°. A numerical absorption correction was applied to the data with the help of the programs X-RED and X-SHAPE [8]. A total of 4229 independent reflections were collected, giving 397 observed reflections with $I > 2\sigma(I)$. The structure was solved by direct method [9] and refined on F^2 by full-matrix least-square using the X-STEP32 program package [10] giving a final $R_1 = 0.0593$, $wR_2 = 0.1444$. The largest peak and hole on the final difference-Fourier map were 0.245 and −0.256 e/Å^{-3}, respectively. Crystal data and structure refinement parameter are listed in Table 1. Selected bond lengths and angles are given in Table 2.

Result and Discussion

An ORTEP [11] drawing and a packing diagram of this compound is shown in Figs. 1 and 2, respectively. The anionic cyanamide groups of azodicyd^{2-} are approximately

Table 1 Crystallographic data and structure Refinement for $[(n\text{-Bu})_4\text{N}]_2[\text{azodicyd}] \cdot \text{H}_2\text{O}$

Molecular formula	$\text{C}_{46}\text{H}_{82}\text{N}_8\text{O}_1$
Molecular weight	781.22
Crystal size (mm)	0.45 × 0.15 × 0.10
Crystal color	Red
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	9.759(3)
b (Å)	11.237(4)
c (Å)	11.919(4)
α (°)	95.54(3)
β (°)	98.50(3)
γ (°)	109.39(2)
V (Å^3)	1204.4(7)
Z	1
D_c (g/cm^3)	1.077
F (000)	432
Goodness of fit on F^2	1.081
Absorption coefficient (mm^{-1})	0.067
Absorption correction $T_{\max}$ and $T_{\min}$	0.995 and 0.985
Largest diff. Peak and hole (e Å^{-3})	0.245 and −0.256
Data/restraints/parameters	4229/0/397
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0593$, $wR_2 = 0.1444$
R indices (all data)	$R_1 = 0.0807$, $wR_2 = 0.1570$

Table 2 Selected bond lengths (Å) and bond angles (°) for $[(n\text{-Bu})_4\text{N}]_2[\text{azodicyd}] \cdot 2\text{H}_2\text{O}$

C(1)–N(1)	1.169(3)	N(1)–C(1)–N(2)	172.6(2)
C(1)–N(2)	1.288(3)	N(2)–C(2)–C(7)	118.4(2)
C(2)–N(2)	1.389(3)	N(2)–C(2)–C(3)	124.5(2)
C(5)–N(3)	1.430(3)	C(4)–C(5)–N(3)	115.9(2)
N(3)–N(3)#1	1.247(4)	C(6)–C(5)–N(3)	125.7(2)

Symmetry transformations used to generate equivalent atoms: #1 −x + 1, −y + 2, −z + 2

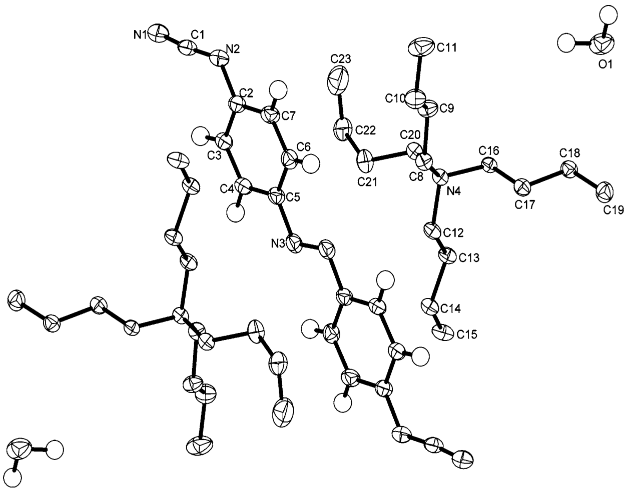

Fig. 1 ORTEP diagram of the $[(n\text{-Bu})_4N]_2$[azodicyd] showing 30% probability ellipsoids [10]. Hydrogen atoms and some atom numbering are omitted for clarity.

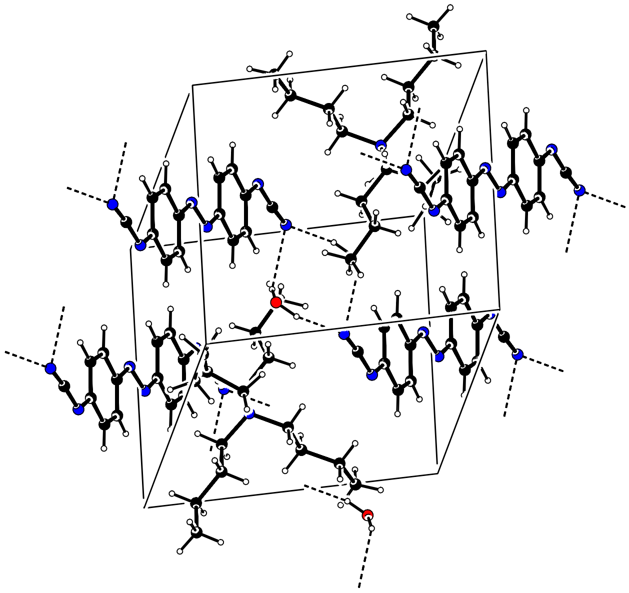

Fig. 2 Crystal packing diagram for this compound and showing hydrogen bonding

linear with the NCN angle of 172.6(2)° as is seen in the coordination to the metal atoms through its terminal nitrogen sites. The study shows that the size of this angle does not change significantly when it is coordinated to the metal atom, such as, for example in some of the Ru- azodicyd^{2-} complexes [12]. In the structure consist of centrosymetric dinuclear units linked by double end to end phenylcyanamido bridges, bond angle range NCN are between 175.5(3)° and 177.0(8)° [13, 14]. The terminal nitrogen to carbon bond length (N1−C1) is 1.169(3). This bond length shows significant triple bond character. The carbon to amide nitrogen bond length (C1–N2) is 1.288(3) showing significant double bond character. This indicates that the bond lengths of the cyanamide group are not simply the average of resonance forms of ($-N{=}C{=}N^- \rightleftarrows -N^- -C{\equiv}N$) and this suggest that carbon in cyanamide possesses hypervalent character. In contrast, the crystal structure of $[\{Ru(terpyridine)(bpy)\}_2(\mu\text{-azodicyd})][PF_6]_2$ showed that its azodicydo terminal nitrogen to carbon bond length is decreased (1.162(7)) but the carbon to amide nitrogen bond length is increased (1.299(8)) [12]. The 1,4-dicyanamidebenzene and its substituted derivatives possess similar cyanamide group bond lengths and angles[15–17].

The cyanamide planes formed by N1–C1–N2 are tilted by only 3.8° with respect to the plane of phenyl rings. The azodicyd^{2-} is approximately planar, with the cyanamide groups in an anti conformation relative to each other and the azo group adopting the more thermodynamically stable trans conformation. The planar geometry of the dianion ligand is suggested to allow for a more effective π-delocalization of the cyanamide groups with phenyl and azo groups. This extensive π conjugation between the cyanamide and azo groups and phenyl ring provides an energetically favorable means by which a metal ion can couple into a conjugated organic π system. In this atomic arrangement, there are two tetrabutylammonium cations per one azodicyd^{2-} anion to ensure the electric neutrality of the total compound and one water molecule in the unit cell. The azodicyd^{2-} anion in the solid state possesses an inversion center, it seems likely that the complex in solution will be able to access a range of possible conformations of lower symmetry, and this will have relevance to the spectroscopic analysis to follow. As Fig. 2 reveals, there is some intermolecular O–H···N [H1A···N1^{i} = 2.42(6), O1···N1^{i} = 2.974(4) Å and O1–H1A···N10^{i} = 115(4)° and H1B···N1^{ii} = 1.97(9), O1···N1^{ii} = 2.858(4) Å and O1–H1B···N1^{ii} = 162(5)°, symmetry codes: (i) −X, 1−Y, 2−Z; (ii) −1+X, Y, −1+Z] hydrogen bonds. Consequently, hydrogen bonds stabilize a one-dimensional network formed with the anion parts that the cations will be laid between these chains (Fig. 3). The presence of hydrogen bonding might be expected to significantly affect other lattice interactions. The O–H groups of water molecule act as hydrogen donors and nitrogen atoms of the azodicyd^{2-} ligand act as acceptors. The potential hydrogen bonds between O–H···N connect azo molecules to form

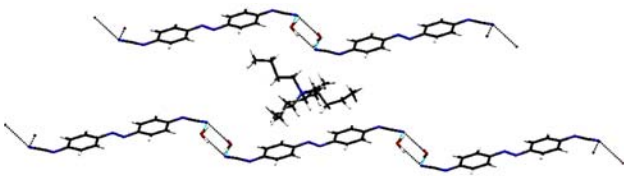

Fig. 3 Fragment of 1D network of hydrogen bonding found in this compound

linear chain structure in crystal structure. Hydrogen bonds seem to de effective in stabilization of the crystal structure.

Electronic spectrum of this compound was taken in different solvents (different dielectric). Electronic spectra of the compound in acetonitrile shows two absorption bands in the UV region and one absorption band in the visible region. The absorption bands centered at 264, 336 nm are assigned to ligand-centered $\pi \rightarrow \pi^*$ transitions. The intense absorption bands centered at approximately 491 nm is assigned to $n \rightarrow \pi^*$ since this band is shifted toward shorter wavelengths (blue shift) in high dielectric solvents, while a red shift was observed for the $\pi \rightarrow \pi^*$ transitions in high dielectric solvents [18].

Supplementary Material

Crystallographic data for the structure reported in this paper have been deposited with the Cambrige Crystallographic Data Center as supplementary publication no. CCDC 605445. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk; url: http://www.ccdc.cam.ac.uk).

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