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تهیه و ساختار بلوری یک کمپلکس شش کوردینهٔ جدید از گالیم (III)

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چکیده: از واکنش گالیم(III) نیترات هشت آبه با سیستم انتقال پروتون -۶،۲ = pyda) (pydaH_r)^{۲+}(pydc)^{۲-} پیریدین دی آمین، ۶،۲ = pydcH_r پیریدین دی کربوکسیلیک اسید) کمپلکس [C₅H₈N₃][Ga(C₇H₃NO₄)₂] · 4H₂O · CH₃OH به دست میآید که دارای ساختار بلوری سه میل، با گروه فضایی Pī و دو مولکول در یاختهٔ یکه است. ابعاد و زاویههای یاخته یکه عبارتند از:

> $a=1 \cdot T \nabla A (1 \nabla) \hat{A}$ $b=1 \cdot F \nabla A \nabla (1 \nabla) \hat{A}$ $c=1 \nabla A \nabla A (\nabla) \hat{A}$ $\alpha = \forall \cdot \forall \forall \Delta(\tau)^{\circ} \qquad \beta = \forall \forall \forall \forall \Lambda(\tau)^{\circ} \qquad \gamma = \forall \forall \forall \forall \Lambda(\tau)^{\circ}$

یس از تعیین ساختار مولکولی، مقدار R تا میزان ۰٬۰۵۷۹ برای ۴۷۰۳ بازتاب کاهش یافت.

واژههایکلیدی: سیستم خود مجموعهساز، ساختار بلوری، پیوندهای هیدروژنی، کمپلکس گاليم(III).



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Synthesis and Crystal Structure of a Novel Six-Coordinate Gallium (III) Complex

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Abstract: The reaction of gallium (III) nitrate octahydrate with the proton transfer compound $(pydaH_1)^{r+} (pydc)^{r-}$ (where pyda is $r \cdot r$ -pyridinediamine and $pydcH_r$ is $r \cdot r$ -pyridinedicarboxylic acid) leads to the formation of $(C \cdot H_A N_r)$ [Ga $(C_v H_r N O_{\epsilon})_r$] · $\epsilon H_r O$ · CH_rOH. The crystal system of the anionic complex is triclinic with space group $P_{\overline{I}}$ and two molecules per unit cell. The unit cell parameters are $a=1\cdot, r r \wedge (r)$ Å, $b=1\cdot, \epsilon r \wedge (r)$ Å, $c=1r, \wedge r \wedge (r)$ Å, $\alpha=v \cdot, r \vee o(r)^\circ$, $\beta=v \vee, q r \wedge (r)^\circ$, $\gamma=\tau \epsilon, 1 \tau \cdot (r)^\circ$. The structure has been refined to a final value for the crystallographic R factor of $\cdot, \cdot \circ \vee q$ based on $\epsilon \vee \cdot r$ reflections with I > $r \sigma(I)$.

Keywords: Self assembling systems, Crystal structure, Hydrogen bonds, Gallium(III) complex.

Introduction

Preparation and characterization of self assembling compounds has been of interest in the recent years $[1, \tilde{T}]$. These self assembling systems are formed through noncovalent interactions. The intermolecular forces in such systems may involve hydrogen bonding, ion pairing, π - π stacking, hydrophobic or hydrophilic, donor-acceptor and host-guest interactions. Often one or a combination of these interactions can result in the formation of specific self assembling systems.

In this regard the proton transfer compound LH₁ (LH₁ is (pydaH₁)^{*+} (pydc)^{*-} where pyda =^{*}(¹-pyridinediamine and pydcH₁ = ^{*}(¹-pyridinedicarboxylic acid) was prepared by our research group previously[[#]]. Several complexes were synthesized using this proton transfer system and their X-ray crystal structures were reported. Some of these complexes possess (pydc)^{*-} ligand and also (pydaH)⁺ fragment, where pyda in its protonated form acts as a counter ion of the anionic complex[^{£-1,•}]. There are also some other complexes of LH₁ in which no counter ion is observed in the structure [^Y, ¹-¹[£]]. Here, we report the synthesis and X-ray crystal structure of Ga(III) complex with the above proton transfer system.

Experimental

An aqueous solution of gallium(III) nitrate octahydrate $(\cdot, \wedge^{q} \cdot g, \cdot, \vee^{r})$ mmol in $\forall \cdot$ mL of water) was added to a solution of LH_r $(\cdot, \vee^{r}) g, \cdot, \vee^{r}$ mmol) in water $(\vee mL)$. The consequent solution was left at room temperature for $\forall \cdot$ hours. The resulting yellow crystals were solved in methanol and suitable crystals for X-ray analysis were obtained after \vee^{r} hours.

Results and discussion

The reaction of LH_r ligand with gallium (III) nitrate octahydrate in a Y:1 molar ratio leads to the formation of the title complex. There is a list of crystal data and structure refinement in the table \. The molecular structure of the compound exhibits a six coordinate anionic complex accompanied by a counter ion. There is also one uncoordinate methanol molecule in the crystal structure as well as four water molecules. Figure 1 illustrates the molecular structure of the title complex. The central ion is coordinated by $tw(pydc)^{r}$ ligands via two O atoms and one N atom from each ligand. The geometry of the complex is distorted octahedral. The two (pydc)^{*-} groups are approximately perpendicular to each other as specified by some of the torsion angles and bond angles. The torsion angles $O(\Lambda)$ —Ga(1)—N(1)—C(T) and $O(\Lambda)$ —Ga(1)—N(1)—C(T) are $-4 \cdot V(T)^{\circ}$ and $(1, \xi)^{\circ}$ respectively. Also the bond angles $O(\xi) - Ga(1) - O(\xi)$ and $O(\Lambda)$ -Ga(1)-O(\pounds) are $\P1, \P0(\P)^\circ$ and $\P1, \PT(\P)^\circ$ respectively (table \P).

Atomic coordinates and equivalent isotropic displacement parameters for the complex are listed in table [•] and anisotropic displacement parameters are collected in table \pounds . The Ga(III) does not lie on a perfect linear axial angle, and the N¹-N⁴ axis shows a variation of 1^4 , \wedge° from linearity. An important feature of the structure is the presence of mono protonated form of 1^4 , 1^4 -pyridinediamine in the compound. This cationic fragment acts as a counter ion and balances the charge. It is interesting to note that we started the reaction with diprotonated form of pyda, while the resulting compound contains pyda in its monoprotonated form. The protonated site of pyda in the product compound is the nitrogen atom of the ring, while in the starting material LH₇, pyda was diprotonated on the nitrogen atoms of the amine groups.

Figure \checkmark illustrates the crystal packing of the title compound. The self assembling system of the compound is formed using hydrogen bonding and ion pairing interactions. These two factors cause the compound to form a three-dimensional network. A wide range of hydrogen bonds from weak to strong interactions are observed in the structure. The presence of four uncoordinated water molecules causes the structure to have a complicated lattice of different hydrogen bonds. Hydrogen coordinates and isotropic displacement parameters for the title complex are listed in Table \circ and a list of hydrogen bonds is collected in Table \checkmark .

The atoms $O({}^{t}W)$, $C({}^{t}S)$ and $O({}^{t}S)$ are disorder atoms. $O({}^{t}W)$ and also $C({}^{t}S)$ atom exhibit three positions, where two positions are illustrated by $O({}^{t}S)$ atom. The distances between different positions of $O({}^{t}W)$ atom are $O({}^{t}W)$ — $O({}^{t}W')$ = ${}^{\bullet},{}^{\bullet}Y \cdot ({}^{t}Y)$ Å and $O({}^{t}W)$ — $O({}^{t}W'')$ = ${}^{\bullet},{}^{V} \wedge ({}^{t}Y)$ Å, and that of the $C({}^{t}S)$ atom are $C({}^{t}S')$ — $C({}^{t}S') = {}^{\bullet},{}^{V}Y \cdot ({}^{t}Y)$ Å and $C({}^{t}S'')$ — $C({}^{t}S') = {}^{\bullet},{}^{\bullet}Y'({}^{t}Y)$ Å. These distances show much more disordering about $O({}^{t}W)$ atom.

Conclusion

The present work supports the strong ability of the LH_r compound in forming the self assembling systems with metal ions. The extensive hydrogen bonding lattice of the metal-organic compound (pydaH)[Ga(pydc)_r] · $t_{\rm HrO}$ · CH_rOH is interesting to note in this regard. The presence of the cationic counter ion (pydaH)⁺ which causes ion pairing interactions in the structure provides a view of expected uncovalent intermolecular forces for the future works.

Acknowledgments

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Figure \ The molecular structure of the title compound.



Figure ^۲ The crystal packing of the title compound.

Empirical formula	CY • HY Ga No O Y
Formula weight	715,18
Temperature	۱۲.(۲) K
Wavelength(λ MoK _{α})	۰,۷۱۰۷۳ Å
Crystal system, space group	Triclinic, Pī
	$a = 1 \cdot , \Upsilon \Lambda(\Upsilon) \text{ Å}$
	$b = 1 \cdot , \epsilon \uparrow \Lambda(\uparrow) Å$
Unit cell dimensions	$c = \mathbf{1T}, \mathbf{ATA}(\mathbf{Y}) \mathbf{A}$
	$\alpha = \forall \cdot, \forall \lor \circ (\forall)^{\circ}$
	$\beta = \forall \forall, 9 \forall \wedge (\forall)^{\circ}$
	$\gamma = 12, 11. (7)^{\circ}$
Volume	۱۲٤٨,٦(٤) Å'
Z, Calculated density	۲, ۱, ۳۴ g/cm ⁺
Absorption coefficient	1,1 [*] mm ⁻
$F(\cdot \cdot \cdot)$	141
Crystal size	۰,۸ _X ۰,۰ _X ۰,٤ mm
Theta range for data collection	۲,۲۲ to ۲۸,۰٤ deg.
Limiting indices	-1 <i>T<h<1t< i="">, -1<i>T<k<1t< i="">, -1<i>A<1<1A</i></k<1t<></i></h<1t<></i>
Reflections collected / unique	$17 \land 97 / 7 \cdot 1 \cdot [R(int) = \cdot, \cdot 7 \circ 9]$
Completeness to theta = $\forall \land, \cdot \notin$	99,1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	$\cdot, \wedge \cdot \uparrow$ and $\cdot, \uparrow \lor \uparrow$
Refinement method	Full-matrix least-squares on F
Data / restraints / parameters	J.I./W/W9W
Goodness-of-fit on F	١,.٨٢
Final R indices [for $tv.r$ refs	$R = \cdot, \cdot \circ \vee \circ, W R = \cdot, 1 \circ \sharp $
with I>Y sigma(I)]	
<i>R</i> indices (all data)	$R^{1} = \cdot, \cdot \forall ? \circ, WR^{2} = \cdot, 1 ? ? \cdot$
Largest diff. peak and hole	1,919 and,090 eÅ-

 Table \ Crystal data and structure refinement of the title complex.

Table ${}^{\varsigma}$ Selected geometric parameters of the title complex (Å, °).

Ga(1)-N(1)	1,901(7)	$N(\gamma)-Ga(\gamma)-O(\gamma)$	۷۹,10(۱۰)
Ga(1)-N(7)	1,909(7)	$N(\gamma)-Ga(\gamma)-O(\epsilon)$	٩٠,٢١(٩)
Ga(1)-O(7)	۱,۹۶۸(۲)	O(7)-Ga(1)-O(7)	95,77(1.)
Ga(1)-O(^)	۲,(۲)	$O(7)$ -Ga(1)-O(ϵ)	۱۵۷,۶۸(۹)
Ga(1)-O(1)	۲,۰۰۰(۲)	$O(7)$ -Ga(1)-O($^{\wedge}$)	91,1.(1.)
Ga(1)-O(t)	۲,۰۷٥(۲)	$O(\mathfrak{t})$ -Ga(\mathfrak{I})-O(\mathfrak{I})	91,70(9)
N(1)-Ga(1)-N(7)	177,7.(1.)	$O(1)-Ga(1)-O(\Lambda)$	107,47(1.)
N(1)-Ga(1)-O(7)	۸۰,٥٧(۱۰)	$O(\Lambda)$ -Ga(1)-O(\mathfrak{t})	91,97(9)
N(1)-Ga(1)-O(1)	۷۷,۲۲ (۹)	O(1)-Ga(1)-N(1)-C(1)	_9 · , ٣(Y)
N(1)-Ga(1)-O(1)	٩٨,٤٣(١٠)	O(1)-Ga(1)-N(1)-C(1)	۸۷,٥(۲)

$N(1)-Ga(1)-O(\Lambda)$	1.7,77(1.)	$O(\Lambda)-Ga(1)-N(1)-C(\Upsilon)$	-9·,V(Y)
$N(\gamma)$ -Ga())-O(γ)	117, (1.)	$O(\Lambda)-Ga(\Lambda)-N(\Lambda)-C(\Lambda)$	٩١,٤(٢)
$N(\gamma)-Ga(\gamma)-O(\Lambda)$	٧٨,٩٤(١٠)		

Table ^r	Atomic	coordinate	es(x \ · ')	and equ	ivalent	isotropic	displacen	nen parameters
(Å'xl•"). U(eq)	is defined	as one th	ird of th	e trace	of the ort	hogonalize	ed <i>Üij</i> tensor.

-1 <t< th=""><th></th><th>r</th><th>12</th><th>7</th><th>U(ea)</th></t<>		r	12	7	U(ea)
State(y) $c + V_1(r)$ $VV_1(r)$ $VV_1(r)$ $VV_1(r)$ $VV_1(r)$ $VV_1(r)$ O(1) $c + V_1(r)$ $VV_1(r)$ $T^{T}_1(r)$ $VV_1(r)$ $T^{T}_1(r)$ $VV_1(r)$ O(1) $c + T_1(r)$ $VV_1(r)$ $T^{T}_1(r)$ $VV_1(r)$ $T^{T}_1(r)$ O(1) $c + T_1(r)$ $VT_1(r)$ $T^{T}_1(r)$ $VV_1(r)$ O(1) $c + T_1(r)$ $VT_1(r)$ $T^{T}_1(r)$ $VV_1(r)$ O(1) $c + T_1(r)$ $VT_1(r)$ $T^{T}_1(r)$ $VV_1(r)$ O(1) $c + T_1(r)$ $VT_1(r)$ $T^{T}_1(r)$ $V^{T}_1(r)$ O(1) $c + T_1(r)$ $VT_1(r)$ $T^{T}_1(r)$ $T^{T}_1(r)$ O(1) $c + T^{T}_1(r)$ $VT_1(r)$ $T^{T}_1(r)$ $T^{T}_1(r)$ O(1) $c + T^{T}_1(r)$ $VT_1(r)$ $T^{T}_1(r)$ $T^{T}_1(r)$ O(2) $c + VV^{T}(r)$ $T^{T}_1(r)$ $T^{T}_1(r)$ $T^{T}_1(r)$ $T^{T}_1(r)$ O(2) $c + VV^{T}(r)$ $T^{T}_1(r)$ $T^{T}_1(r)$	Ga(l)	A 0793(1)	y Y9.9(1)	2	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N(1)		۲۷٤٠(۳)	7901(7)	ΥΛ(1)
O(1) $I + I + V(1)$ $I + I + V(1)$ $I + V(1)$ $I + V(1)$ $O(1)$ $I + I + V(1)$ $I + I + V(1)$ $I + V(1)$ $I + V(1)$ $O(1)$ $I + I + V(1)$ $I + I + V(1)$ $I + I + V(1)$ $I + V(1)$ $O(1)$ $I + I + V(1)$ $I + I + V(1)$ $I + I + V(1)$ $I + V(1)$ $O(1)$ $I + V + V(1)$ $I + I + V(1)$ $I + I + V(1)$ $I + V(1)$ $O(1)$ $I + V + V(1)$ $I + I + V(1)$ $I + V + V(1)$ $I + V(1)$ $O(1)$ $I + V + V(1)$ $I + I + V + V(1)$ $I + V + V + V(1)$ $I + V + V + V + V + V + V + V + V + V +$	$\Omega(1)$	4700(7)	٥٣٩٨(٣)	** (*)	£ (1)
C(1) LTT(1) TTT(1) TTT(1) TTT(1) O(1) -TT1(1) TT1(1) TT1(1) TT1(1) N(1) -LT1(1) TT1(1) TT1(1) TT1(1) N(1) -LT1(1) TT1(1) TT1(1) TT1(1) N(1) -LT1(1) TT1(1) TT1(1) TT1(1) O(1) -VTTV(1) LT1(1) TT1(1) TT1(1) O(1) -VTTV(1) LT1(1) VTV1(1) TT1(1) O(1) -VTTV(1) TT1(1) VTV1(1) TT1(1) O(1) -VTV1(1) TT1(1) VTV1(1) TT1(1) O(1) -VTV1(1) TT1(1) TT1(1) T1(1) O(1) -VTV1(1) TT1(1) T11(1) T11(1) O(1) -VTV1(1) T11(1) T11(1) T11(1) O(1) -TT1(1) T11(1) T11(1) T11(1) O(1) -TT1(1) T11(1) T11(1) T11(1) O(1) -TT1(1) T11(1) T11(1)	$C(\mathbf{Y})$	<u> </u>	<u> </u>	£11£(Y)	YY (1)
O(t) L111(t) L111(t) L111(t) L111(t) $C(i)$ -1APT(i) TITT(T) P4PA(T) TT(i) $C(i)$ -1APT(i) TTTT(T) P4PA(T) TT(i) $O(T)$ -VTTV(T) ITTT(T) TTTT(T) TTT(I) $O(T)$ -VTTV(T) ITTT(T) PTTT(T) TTT(I) $O(T)$ -VTTA(T) TTTT(T) PTTT(T) TTT(I) $O(T)$ -VTAA(i) TTTT(T) PTTT(T) TTT(I) $O(T)$ -VTAA(i) TTTTT(T) PTTTT(T) TTT(I) $O(T)$ -VAAA(i) TTTTT(T) PTTTTT(T) TTT(I) $O(T)$ -VAAA(T) ISTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTT	$C(\tau)$		184.(8)	**	
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N(1)	$\mathcal{L}(\mathbf{z})$		1211(1)		
$O(1)$ $-r(Y_1(1)$ $T(Y_1(1)$ $T(Y_1(1)$ $T(Y_1(1)$ $C(T)$ $-et \cdot (T)$ $Tite(T)$ $et Y_1(T)$ $T(T)$ $O(T)$ $-reto(T)$ $Tite(T)$ $et Y_1(T)$ $T(T)$ $O(T)$ $-reto(T)$ $Tite(T)$ $et Y_1(T)$ $To(T)$ $O(T)$ $-reto(T)$ $Tite(T)$ $et Y_1(T)$ $To(T)$ $O(T)$ $-et Y_1(T)$ $Tot(T)$ $Tr(T)$ $To(T)$ $O(T)$ $-et Y_1(T)$ $Tot(T)$ $Tr(T)$ $To(T)$ $O(T)$ $-et Y_1(T)$ $Tot(T)$ $Tr(T)$ $To(T)$ $O(T)$ $-et Y_1(T)$ $Tot(T)$ $Tit(T)$ $To(T)$ $O(e)$ $-et Y_1(T)$ $1e TT_1(T)$ $Tot(T)$ $To(T)$ $O(t)$ $-et Y_1(T)$ $Tot(T)$ $To(T)$ $To(T)$ $O(t)$ $-TTT_1$	$N(\tau)$		· · · · · (·)		
C(1) $-2 \cdot 2 \cdot 1 (1)$ $11 \cdot 2 \cdot 1 (1)$ $21 \cdot 1 \cdot 1 (1)$ $21 \cdot 1 \cdot 1 (1)$ O(7) $-7 \cdot 4 \cdot \delta \cdot (T)$ $11 \cdot 4 (T)$ $21 \cdot 1 \cdot (T)$ $7 \cdot 0 \cdot (T)$ C(a) $-7 \cdot A \cdot A \cdot (E)$ $7 \cdot E \cdot T (T)$ $0^{T} \cdot 0 \cdot (T)$ $T \cdot T (T)$ O(7) $-2^{T} \cdot V \cdot V (T)$ $T \cdot T \cdot T (T)$ $2^{T} \cdot V \cdot T (T)$ $T \cdot T \cdot T (T)$ O(7) $-2^{T} \cdot V \cdot V (T)$ $T \cdot T \cdot T (T)$ $T \cdot T \cdot$		- • • • • • • • • • • • • • • • • • • •	21 (2(1))		
$0(1)$ $-1 t A O(1)$ $1 Y (Y)$ $2 Y Y Y (Y)$ $1 Y Y Y Y Y$ $C(2)$ $-V A \cdot A (1)$ $Y Y Y Y (Y)$ $2 Y Y \cdot P(Y)$ $Y Y Y Y (Y)$ $T O(1)$ $O(1)$ $-2 V Y \cdot Y (Y)$ $1 Y V Y (Y)$ $T Y Y Y (Y)$ $T O(1)$ $C(1)$ $-V Y V Y (Y)$ $T 2 t Y (Y)$ $T Y Y A (Y)$ $T O(1)$ $C(1)$ $-V Y V Y (Y)$ $T 2 t Y A (Y)$ $T Y Y A (Y)$ $T O(1)$ $O(2)$ $-A \cdot A T (Y)$ $1 Y Y (Y)$ $T Y A (Y)$ $T Y (1)$ $O(2)$ $-A \cdot A T (Y)$ $1 Y Y (Y)$ $T O (1)$ $O(2)$ $-P Y V (t)$ $-Y = A (Y)$ $Y = A (Y)$ $O(1)$ $-Y = A (Y)$ $1 Y Y (Y)$ $Y = A (Y)$ $O(1)$ $-Y = A (Y)$ $1 Y = A (Y)$ $Y = A (Y)$ $O(1)$ $-Y = A (Y)$ $1 Y = A (Y)$ $Y = A (Y)$ $O(1)$ $-Y = A (Y)$ $1 Y = A (Y)$ $Y = A (Y)$ $O(1)$ $-Y = A (Y)$ $Y = A (Y)$ $Y = A (Y)$ $O(1)$ $-Y = A (Y)$ $Y = A (Y)$ $Y =$	$C(\tau)$	-52::(1)			
C(e) $\cdot \forall \forall \cdot (t)$ $\forall \forall \forall \forall \forall (t)$ $\forall \forall \forall \forall \forall \forall (t)$ $\forall \forall \forall (t)$ O(1) $- \circ \forall \forall \cdot (t)$ $\forall \forall \forall \forall \forall (t)$ $\forall \forall \forall \forall \forall (t)$ $\forall \forall \forall \forall (t)$ C(1) $- \forall \forall \forall (t)$ $\forall \forall \forall \forall (t)$ $\forall \forall \forall \forall (t)$ $\forall \forall (t)$ C(1) $- \forall \forall \forall (t)$ $\forall \forall \forall \forall (t)$ $\forall \forall \forall (t)$ $\forall \forall (t)$ C(1) $- \forall \forall \forall (t)$ $\forall \forall \forall (t)$ $\forall \forall (t)$ $\forall \forall (t)$ O(0) $- \forall \forall \forall (t)$ $1 \forall \forall (t)$ $\forall \forall (t)$ $\forall \forall (t)$ O(1) $- \forall \forall \forall (t)$ $1 \forall \forall (t)$ $\forall \forall (t)$ $\forall (t)$ O(1) $- \forall \forall \forall (t)$ $1 \forall \forall (t)$ $1 \forall (t)$ $\forall \forall (t)$ O(1) $- \forall \forall \forall (t)$ $1 \forall \forall (t)$ $1 \forall \forall (t)$ $\forall \forall (t)$ O(1) $- \forall \forall \forall (t)$ $1 \forall \forall (t)$ $1 \forall \forall (t)$ $0 \forall (t)$ C(1) $- \forall \forall (t)$ $1 \forall \forall (t)$ $1 \forall \forall (t)$ $1 \forall (t)$ $0 \forall (t)$ C(1) $- \forall \forall \forall (t)$ $1 \forall \forall (t)$ $1 \forall \forall (t)$ C(1) $- \forall \forall \forall (t)$ $1 \forall \forall (t)$ $1 \forall (t)$ <td< td=""><td>O(r)</td><td>-12/0(1)</td><td></td><td>2 4 2 . (1)</td><td>f^b(1)</td></td<>	O(r)	-12/0(1)		2 4 2 . (1)	f ^b (1)
$O(t)$ $-\delta V V \cdot (t)$ $V V V (t)$ $T \delta t A (T)$ $T \delta t A (T)$ $T \delta t A (T)$ $C(t)$ $-V V V A (T)$ $T \delta t A (T)$ $t V V V (t)$ $T \delta t A (T)$ $T \delta t A (T)$ $C(t)$ $-A \cdot A T (T)$ $t \delta T T (T)$ $T V V A (T)$ $T \delta t A (T)$ $O(t)$ $-\delta V V (t)$ $-T \delta A (t)$ $1 t \cdot T (T)$ $T T (t)$ $O(t)$ $-T T \cdot I (T)$ $\delta T V (T)$ $A \cdot \delta (T)$ $T A (t)$ $O(t)$ $-T T \cdot I (T)$ $\delta T V (T)$ $V \cdot \delta (T)$ $T A (t)$ $O(t)$ $-T T \cdot I (T)$ $\delta T V (T)$ $V \cdot \delta (T)$ $T A (t)$ $O(t)$ $-T T \cdot I (T)$ $\delta T V (T)$ $V \cdot \delta (T)$ $T A (t)$ $O(t)$ $-T T \cdot I (T)$ $1 T T T (T)$ $T T (T)$ $T T (T)$ $C(1)$ $-T T \cdot I (t)$ $T T T A (t)$ $T T T A (t)$ $T T T (T)$ $T T (T)$ $C(1)$ $-T T + I (t)$ $T T T A (t)$ $T T T T (T)$ $T T (T)$ $C(1)$ $-T T + I (t)$ $T T T (T)$ $T T (T)$ $T T T (T)$	C(*)	- • • • • (2)	F2FF(F)	87.8(7)	ff(1)
C(1) -VVV(T) $P \circ I (T)$ $I \wedge T(T)$ $T \cdot (1)$ C(V) - $\Lambda \cdot \Lambda T(T)$ $I \circ T T(T)$ $T T \wedge T(T)$ $T \circ (1)$ O(0) - $0 \vee V(I)$ $-T \circ \Lambda(I)$ $I I \cdot T(T)$ $T T \cdot (1)$ C(I) - $T I \wedge T(T)$ $V \cap T(T)$ $I \wedge V(I)$ $V \cap T \cdot (1)$ O(0) - $T T \cdot T(T)$ $0 \vee T \cap T(T)$ $I \wedge V(I)$ $V \cap T \cdot (1)$ O(A) - $I \circ V \circ (T)$ $I \vee T \vee T(T)$ $V \cap T \vee T \cdot (1)$ $V \cap T \circ (1)$ O(A) - $I \circ V \circ (T)$ $I \vee T \vee T(T)$ $I \vee T \vee T \cap T \circ (1)$ $V \cap T \cap T \circ (1)$ O(A) - $I \circ V \circ (T)$ $I \vee T \vee T \cap T \cap T \circ T \circ (1)$ $T \vee T \circ (1)$ $T \vee T \circ (1)$ C(1) - $I \vee T \vee T \cap I \cap T \circ T \cap I \cap T \circ T \cap T \cap T \circ T \cap T \circ T \cap T \cap T \circ T \cap T \cap$	O(1)	-07.(1)	1177(7)	TTYT(T)	F°(1)
$C(Y)$ $-\Lambda \cdot \Lambda'(Y)$ $I \Rightarrow T(Y)$ $T \forall T \Lambda(Y)$ $T \circ (1)$ $O(\bullet)$ $-0 \forall V(t)$ $-\nabla \circ \Lambda(t)$ $1 t \cdot T(Y)$ $T'(1)$ $C(I)$ $-T \forall t \Lambda T(Y)$ $1 \cdot T \cdot T(Y)$ $t \dagger \Lambda V(Y)$ $V'(1)$ $O(V)$ $-T T \cdot \Lambda(T)$ $0 \top I V(T)$ $\Lambda \cdot o(Y)$ $0 \lor (1)$ $O(\Lambda)$ $-I \Leftrightarrow V \circ (T)$ $I \lor T \lor T \cdot V(T)$ $I \land \Lambda (I)$ $T \lor (I)$ $O(\Lambda)$ $-I \Leftrightarrow V \circ (T)$ $I \lor T \land V \circ (T)$ $T \land \Lambda (I)$ $T \lor (I)$ $O(\Lambda)$ $-I \Leftrightarrow V \circ (T)$ $I \lor I \land I \land V \circ (T)$ $T \land \Lambda (I)$ $T \lor (I)$ $C(1 \cdot I)$ $-T \lor T \land T \cap (I)$ $I \lor I \land I \land I \circ I \to T \land T \land (I)$ $T \land I \land I \circ I \to T \land I \land I \circ I \to T \land I \land I \land I \to T \land I \land I \land I \to T \land I \land I \to T \land I \land I \to T \land I \land I \to I \land I \land I \to I \land I \land I \to I \land I \land$	C(1)		۳٥٤٩(٣)	£1AT(T)	۳.(۱)
$O(\circ)$ $-201VV(\dot{z})$ $-70A(\dot{z})$ $1\dot{z}.7(T)$ $77(1)$ $C(l)$ $-FtAT(T)$ $1.F.(T)$ $\dot{z}1AV(T)$ $77(1)$ $O(V)$ $-FT \cdot 1(T)$ $\dot{v}1V(T)$ $\dot{v}.o(T)$ $\dot{v}V(1)$ $O(A)$ $-\dot{z}0Vo(T)$ $\dot{z}0To(T)$ $T.oT(T)$ $TA(1)$ $O(A)$ $-\dot{z}0Vo(T)$ $\dot{z}0To(T)$ $T.oT(T)$ $TA(1)$ $C(1)$ $-\dot{z}TT.(\dot{z})$ $1Y\overline{4}Y(o)$ $-FT(T)$ $\dot{z}0(1)$ $C(1)$ $-TTTTT(\dot{z})$ $TT\overline{4}YT(\dot{z})$ $TTO(0)$ $\dot{z}0(1)$ $C(1)$ $-TTTTT(\dot{z})$ $TT\overline{4}YT(\dot{z})$ $TTO(0)$ $\dot{z}0(1)$ $C(1)$ $-TT\overline{4}YT(\dot{z})$ $TT\overline{4}Y(\dot{c})$ $-TTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTT$	C(v)	-^.^(*)	2077(7)	****(*)	۳۰ (۱)
$C(l)$ $-\Psi \xi \Lambda \Psi(\Psi)$ $1 \cdot \Psi \cdot (\Psi)$ $\xi 1 \Lambda \Psi(\Psi)$ $Y q(1)$ $O(V)$ $-\Psi \Psi \cdot \Lambda(\Psi)$ $0 T 1 \Psi (\Psi)$ $\Lambda \cdot o(\Psi)$ $0 \Psi (1)$ $O(\Lambda)$ $-\xi 0 \Psi o(\Psi)$ $\xi 0 \Psi o(\Psi)$ $1 \Psi e \Psi (\Psi)$ $\Psi A(1)$ $C(\Lambda)$ $-\xi 0 \Psi o(\Psi)$ $\xi 0 \Psi o(\Psi)$ $1 \Psi e \Psi (\Psi)$ $\Psi A(1)$ $C(\Lambda)$ $-\xi 0 \Psi o(\Psi)$ $1 \Psi e \Psi e \Psi (\Psi)$ $1 \Psi e \Psi e \Psi (\Psi)$ $\Psi e \Psi (\Psi)$ $C(\Lambda)$ $-\Psi \Psi \Psi \Psi e \Psi$	O(•)	-01VV(£)	-Y • ^(£)	۱٤٠٦(٢)	(۱)
$O(V)$ $-YY \cdot I(Y)$ $\delta \cdot IY(Y)$ $A \cdot \delta(Y)$ $\delta Y(1)$ $O(A)$ $- \delta \delta Y \delta(Y)$ $\delta \delta T \delta(Y)$ $Y \cdot \delta Y(Y)$ $Y \wedge (1)$ $C(A)$ $- \delta Y V \delta(Y)$ $1 \delta \Phi \delta(\xi)$ $A \xi A(Y)$ $Y \circ (1)$ $C(A)$ $- T Y \wedge (Y)$ $1 \delta \Phi \delta(\xi)$ $- T Y (Y)$ $\xi \circ (1)$ $C(A)$ $- T Y \wedge (\xi)$ $1 Y \Phi Y (\bullet)$ $- T Y \cdot (Y)$ $\xi \circ (1)$ $C(A)$ $- T Y Y Y (\xi)$ $Y \Phi \Phi (\bullet)$ $- T Y \cdot (Y)$ $\xi Y (1)$ $C(A)$ $- T Y Y (\xi)$ $Y \Phi \Phi (\bullet)$ $- T Y \cdot (Y)$ $\xi Y (1)$ $C(A)$ $- T Y A + (\xi)$ $T Y \Phi \Phi (\bullet)$ $- Y Y \cdot (Y)$ $Y Y (1)$ $C(A)$ $- \delta Y Y (Y)$ $T Y + Y + (\xi)$ $T Y Y + Y + (\xi)$ $T Y + Y + (\xi)$ $C(A)$ $- \delta Y Y + (\xi)$ $T Y + Y + (\xi)$ $T Y + Y + (\xi)$ $T Y + Y + (\xi)$ $C(A)$ $- \delta Y Y + (\xi)$ $T Y + Y + (\xi)$ $T Y + Y + (\xi)$ $T Y + (Y)$ $C(A)$ $- Y + Y + (\xi)$ $T Y + Y + (\xi)$ $T Y + (Y)$ $\xi Y + (Y)$ $C(A)$ $Y + Y + (\xi)$	C(l)	-***(*)	۱۰۳۰(۳)	٤ ١٨٧(٢)	۲۹(۱)
$O(\Lambda)$ $-i \circ V \circ (V)$ $i \circ V \circ (V)$ $V \cdot \circ V(V)$ $V \cdot \circ V(V)$ $V \wedge (V)$ $C(\Lambda)$ $-i \forall V \wedge (V)$ $1 \circ \eta i (i)$ $\Lambda i \wedge (V)$ $V \circ (V)$ $C(\Lambda)$ $-i \forall V \wedge (V)$ $V \vee (V)$ $i \circ (V)$ $V \circ (V)$ $C(\Lambda)$ $-V \vee V \vee (V)$ $i \circ (V)$ $V \vee (V)$ $i \circ (V)$ $C(\Lambda)$ $-V \vee V \vee V \circ (V)$ $V \vee (V)$ $i \vee V \vee V \vee V \vee V$ $i \circ (V)$ $C(\Lambda)$ $-V \vee V \vee V \circ V \circ (I)$ $i \circ (V)$ $V \vee V \vee$	O(Y)	- 5 . 1 (7)	0717(77)	٨٠٥(٢)	•۷(۱)
$C(4)$ $-\pounds Y T A(T)$ $1 \circ 4 \pounds (\pounds)$ $A \pounds A(Y)$ $T \circ (1)$ $C(1 \cdot)$ $-T Y \xi \cdot \cdot (\pounds)$ $1 Y 4 Y (\circ)$ $-T T T T Y T ()$ $\pounds \circ (1)$ $C(1)$ $-T Y Y T (\pounds)$ $Y 1 \circ 4 (\circ)$ $-T T T (T)$ $\delta Y (1)$ $C(1 Y)$ $-T Y 4 \cdot (\pounds)$ $T Y 4 \cdot (\circ)$ $-T Y \cdot (Y)$ $\pounds T (1)$ $C(1 Y)$ $-T Y 4 \cdot (\pounds)$ $T Y 4 \cdot (\bullet)$ $-T Y \cdot (Y)$ $\pounds T (1)$ $C(1 Y)$ $-T 4 \cdot 1(\pounds)$ $\pounds T Y \pm (\pounds)$ $1 \circ 7 (Y)$ $T T (1)$ $C(1 Y)$ $-T 0 \circ 4(T)$ $T \circ T Y \pm (\pounds)$ $1 \circ 7 (Y)$ $T T (1)$ $C(1 \xi)$ $-T 4 \cdot 1(\pounds)$ $\pounds T Y \pm (\pounds)$ $1 \circ 7 (Y)$ $F A (1)$ $C(1 \xi)$ $-T A \cdot 1(\pounds)$ $\pounds T Y \pm (\pounds)$ $1 \circ A \pm (T)$ $\pounds A (1)$ $C(1 4)$ $-T A (1 + E + E + E + E + E + E + E + E + E + $	O(^)	-±°V°(*)	٤٥٣٥(٢)	۲۰۵۲(۲)	۳۸(۱)
$C(1 \cdot)$ $-rt \cdot \cdot (t)$ $1 r 4 r (0)$ $-rr (r)$ $t 0 (1)$ $C(1)$ $-r 1 r r (t)$ $r 1 0 4 (0)$ $-0 1 r (r)$ $0 r (1)$ $C(1)$ $-r 1 1 4 \cdot (t)$ $r 1 0 4 (0)$ $-r r (r)$ $t r (1)$ $C(1 r)$ $-r 0 0 4 (r)$ $r 0 r t (t)$ $r 0 r (t)$ $r r (1)$ $C(1 r)$ $-r 0 0 4 (r)$ $r 0 r t (t)$ $r 0 r (t)$ $r r (1)$ $C(1 r)$ $-r 0 0 4 (r)$ $r 0 r t (t)$ $r 0 r (t)$ $r r (1)$ $C(1 r)$ $-r 0 0 4 (r)$ $r 0 r t (t)$ $r 0 r (t)$ $r r (1)$ $C(1 r)$ $-r 0 0 4 (r)$ $r 0 r t (t)$ $r 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1$	C(4)	- * * * * (*)	1095(5)	$\Lambda \notin \Lambda(\Upsilon)$	۳۰ (۱)
$C(1)$ $-Y1YY(t)$ $Y104(0)$ $-0TY(T)$ $0Y(1)$ $C(1Y)$ $-Y14\cdot(t)$ $YY4\cdot(0)$ $-YY\cdot(T)$ $tY(1)$ $C(1Y)$ $-Y004(T)$ $T0Tt(t)$ $T0Tt(t)$ $T0T(T)$ $C(1t)$ $-T004(T)$ $T0Tt(t)$ $10A(T)$ $TT(1)$ $C(1t)$ $-T004(T)$ $T0Tt(t)$ $10At(T)$ $TA(1)$ $C(1t)$ $-TAA\cdot1(t)$ $tTTt(t)$ $10At(T)$ $t\cdot(1)$ $C(1t)$ $-TAA\cdot1(t)$ $tTTtt(t)$ $10At(T)$ $t\cdot(1)$ $C(14)$ $-TVA(t)$ $TTTY(T)$ $t\cdot(1)$ $C(14)$ $T\cdot(t)$ $-TtV(t)$ $TTTY(T)$ $tY(1)$ $C(14)$ $TV(t)$ $-TtV(t)$ $TTTY(T)$ $tY(1)$ $C(14)$ $TV(t)$ $-TtV(t)$ $TTTY(T)$ $tY(1)$ $C(14)$ $TV(t)$ $-TtV(t)$ $TTTY(T)$ $tY(1)$ $C(14)$ $TVT(t)$ $-TTTY(t)$ $tTTTY(T)$ $tY(1)$ $C(14)$ $TVT(t)$ $-TTTY(t)$ $tTTTY(T)$ $tY(1)$ $C(15)$ $TTTT(t)$ $-TTTTY(T)$ $tTTTY(T)$ $tTTTY(T)$ $C(17)$ $TTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTT$	$C(1 \cdot)$	- " : • • (:)	1797(0)	- " " (")	٤٥(١)
$C(1Y)$ $-Y14 \cdot (t)$ $YY4 \cdot (0)$ $-YY \cdot (Y)$ $tY(1)$ $C(1Y)$ $-Y004(Y)$ $Y07t(t)$ $101(Y)$ $YY(1)$ $C(1t)$ $-YA \cdot 1(t)$ $t11t(t)$ $10A(Y)$ $YA(1)$ $C(1t)$ $-01YY(t)$ $VY1(t)$ $10A(Y)$ $t \cdot (1)$ $C(14)$ $-01YY(t)$ $VY1(t)$ $10At(Y)$ $t \cdot (1)$ $C(14)$ $Y \cdot (t)$ $-YtV \cdot (t)$ $111V(Y)$ $t \cdot (1)$ $C(14)$ $Y \cdot (t)$ $-YtV \cdot (t)$ $111V(Y)$ $t \cdot (1)$ $C(14)$ $Y \cdot (t)$ $-YtV \cdot (t)$ $111V(Y)$ $t \cdot (1)$ $C(14)$ $Y \cdot (t)$ $-TtV \cdot (t)$ $111V(Y)$ $t \cdot (1)$ $C(14)$ $Y \cdot (t)$ $-TtV \cdot (t)$ $111V(Y)$ $t \cdot (1)$ $C(14)$ $Y \cdot (t)$ $-TtV \cdot (t)$ $111V(Y)$ $t \cdot (1)$ $C(15)$ $YVT(t)$ $-TtV \cdot (t)$ $111V(Y)$ $t \cdot (1)$ $C(15)$ $111V(Y)$ $-111Y(Y)$ $-111Y(Y)$ $t \cdot (1)$ $N(Y)$ $-111Y(Y)$ $-114YA(t)$ $111tO(Y)$ $t \cdot (1)$ $N(Y)$ $-111Y(Y)$ $-114YA(t)$ $11YOA(Y)$ $t \cdot (1)$ $O(W)$ $NYt(Y)$ $-11YOO(Y)$ $YTYV(Y)$ $t \cdot (1)$ $O(W)$ $YYtYY(Y)$ $-11YY(Y)$ $-11YYY(Y)$ $t \cdot (1)$ $O(W)$ $YYtYY(Y)$ $-11YYY(Y)$ $YYYYY(Y)$ $t \cdot (1)$ $O(W)$ $YYYYYYY(Y)$ $-11YYY(Y)$ $YYYYYYYYYYYYYYYYYYYYYYYYYYYYYYYYYYYY$	C(1)	-7777(2)	۲۱٥٩(٥)	-•٦٣(٣)	٥٢(١)
$C(1\Psi)$ $-\Psi \circ \circ \P(\Psi)$ $\Psi \circ \Psi i (i)$ $T \circ T(Y)$ $\Psi \Psi(1)$ $C(1i)$ $-\Psi \wedge \cdot 1(i)$ $i \exists \exists \exists i i (i)$ $11 \wedge \wedge (\Psi)$ $\Psi \wedge (1)$ $C(\Lambda)$ $-\circ 1 \Psi \Psi(i)$ $V \forall \exists i (i)$ $10 \wedge h (\Psi)$ $i \cdot (1)$ $C(\Lambda)$ $-\circ 1 \Psi \Psi(i)$ $V \forall \exists i (i)$ $10 \wedge h (\Psi)$ $i \cdot (1)$ $C(14)$ $\Psi \cdot \cdot (i)$ $-\Psi i \forall \vee (i)$ $11 \forall \Psi (\Psi)$ $i \vee (1)$ $C(1\Lambda)$ $1i i i \cdot (i)$ $-\Psi i \forall \vee (i)$ $11 \forall \Psi (\Psi)$ $i \vee (1)$ $C(1\Lambda)$ $1i i i \cdot (i)$ $-\Psi i \forall \vee (i)$ $11 \forall \Psi (\Psi)$ $i \vee (1)$ $C(1V)$ $\Psi \forall 1 \exists i (i)$ $-i \circ e \P(i)$ $1 \cdot h \circ (\Psi)$ $i \vee (1)$ $C(1V)$ $\Psi \forall 1 \forall (i)$ $-\Psi i \forall \wedge (i)$ $0 \cdot \forall \wedge (\Psi)$ $i \vee (1)$ $C(1V)$ $\Psi \forall 1 \forall (i)$ $-\Psi i \forall (i)$ $0 \cdot \forall \wedge (\Psi)$ $i \vee (1)$ $C(1V)$ $\Psi \forall 1 \forall (i)$ $-\Psi i \forall \wedge (i)$ $0 \cdot \forall \wedge (\Psi)$ $\Psi (1)$ $C(1V)$ $\Psi \forall \pi (i)$ $-\Psi i \forall \pi (i)$ $i \vee (\Psi (i))$ $\Psi (1)$ $N(\Psi)$ $1 \forall \neg (\Psi)$ $-1 \forall \forall \wedge (i)$ $1 \forall i \land (\Psi)$ $\Psi (1)$ $N(\Psi)$ $1 \forall \forall (\Psi)$ $-1 \forall \forall (\Psi)$ $1 \forall (\Psi)$ $\Psi (1)$ $N(\Psi)$ $1 \forall \forall (\Psi)$ $1 \forall \forall (\Psi)$ $1 \forall (\Psi)$ $1 \land (\Psi)$ $N(\Psi)$ $-\Psi e \forall (\Psi)$ $-\Psi e \forall (\Psi)$ $1 \forall (\Psi)$ $1 \land (\Psi)$ $N(\Psi)$ $-\Psi e \forall (\Psi)$ $1 \forall (\Psi)$ $1 \forall (\Psi)$ $1 \land (\Psi)$ $N(\Psi)$ $-\Psi e \forall (\Psi)$ $1 \forall (\Psi)$ $1 \forall (\Psi)$ $1 \forall (\Psi)$ $N(\Psi)$ $1 \forall (\Psi)$ $1 \forall (\Psi)$ $1 \forall (\Psi)$ $1 \forall (\Psi)$ $N(\Psi)$ $1 \forall (\Psi)$ <td>C(1Y)</td> <td>-779.(2)</td> <td>۳۲۹.(۵)</td> <td>-**(*)</td> <td>٤٣ (١)</td>	C(1Y)	-779.(2)	۳۲۹.(۵)	-**(*)	٤٣ (١)
$C(1 \pm)$ $-r \wedge \cdot 1(\pm)$ $\pm 1 \uparrow \pm (\pm)$ $1 \uparrow \wedge \wedge (r)$ $r \wedge (1)$ $C(\Lambda)$ $-0 \uparrow r r (\pm)$ $V \lor \uparrow (\pm)$ $1 \circ \wedge \pm (r)$ $\pm \cdot (1)$ $C(\Lambda)$ $1 \circ \uparrow r r (\pm)$ $-r \pm v \lor (\pm)$ $1 \uparrow \uparrow \lor r r r r r r r r r r r r r r r r r$	C(17)	-8004(2)	۳٥٣٤(٤)	۲۵٦(۲)	۲۳(۱)
$C(\Lambda)$ $-01YY(t)$ $VVT(t)$ $10\Lambda t(Y)$ $t \cdot (1)$ $C(14)$ $Y \cdot \cdot (t)$ $-YtV \cdot (t)$ $11TV(Y)$ $t \cdot (1)$ $C(1\Lambda)$ $1tt (t)$ $-YtV \cdot (t)$ $11TV(Y)$ $t \cdot (1)$ $C(1\Lambda)$ $1tt (t)$ $-ToTA(t)$ $1TTY(Y)$ $tY(1)$ $C(1V)$ $YVTT(t)$ $-ToTA(t)$ $TTAP(Y)$ $tY(1)$ $C(1V)$ $YVTT(t)$ $-TtAV(t)$ $0 \cdot YA(Y)$ $tY(1)$ $C(1T)$ $YATA(t)$ $-TTAV(t)$ $0 \cdot YA(Y)$ $t1(1)$ $C(10)$ $1TTY(t)$ $-TTAV(t)$ $0 \cdot YA(Y)$ $t1(1)$ $N(Y)$ $TTY(t)$ $-TTAV(t)$ $t0 \cdot YV(Y)$ $TA(1)$ $N(Y)$ $TTY(t)$ $-14TA(Y)$ $0 \cdot YV(Y)$ $TA(1)$ $N(Y)$ $TTY(T)$ $-14TA(Y)$ $0 \cdot YV(Y)$ $TA(1)$ $N(t)$ $-111T(T)$ $-14TA(T)$ $11tO(Y)$ $TA(1)$ $N(t)$ $-111T(T)$ $-14TA(T)$ $TTTOV(Y)$ $tA(1)$ $O(IW)$ $NTt(Y)$ $-11TT(T)$ $-14TA(T)$ $TTTOV(Y)$ $O(W)$ $VTA(T)$ $-1VOO(T)$ $TTTTT(Y)$ $tA(1)$ $O(W)$ $VTA(T)$ $-1VT(T)$ $-1VOA(Y)$ $O(T)$ $O(W)$ $-TOOV(4)$ $VVTT(A)$ $tTO(T)$ $TT(t)$ $O(W)$ $-1VOV(4)$ $VVTT(A)$ $tTO(T)$ $TT(t)$ $O(W)$ $-1VOV(4)$ $VVTT(A)$ $tO(Y)$ $V(Y)$ $O(W)$ $-1VOV(4)$ $VVTT(A)$ $tO(Y)$ $V(Y)$ $O(W)$ $-1VOV(4)$ $VTT(Y)$ $TTT(T)$ $TT(t)$ $O(W)$ <td>C(1 ٤)</td> <td>-34.1(2)</td> <td>£77£(£)</td> <td>۱۱۸۸(۳)</td> <td>۳۸ (۱)</td>	C(1 ٤)	-34.1(2)	£77£(£)	۱۱۸۸(۳)	۳۸ (۱)
$C(14)$ $Y \cdot \cdot (i)$ $-Y i V \cdot (i)$ $T 1 T V(T)$ $i 1 (1)$ $C(14)$ $1 i i i \cdot (i)$ $-T \circ T A(i)$ $T T T T T T T T T T T T T T T T T T T $	C (^)	-0177(2)	۷۷٦ (٤)	۱۰۸٤(٣)	٤ •(١)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	C(19)	۲۰۰(٤)	-7 5 7 • (5)	۳)۲۱۲۷)	٤ ١(١)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	C(1^)	۱ ٤ ٤ • (٤)	-٣٥٦٨(٤)	۳)۳۲۲۲	٤٧(١)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	C(1V)	۲۷۱٦(٤)	-± · • ٩(٤)	۲۰۸۵(۳)	٤٣(١)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	C(17)	۲۸۳۸(٤)	-WEAV(E)	۰۰۲۸(۳)	٤١(١)
N(r) $r r r r (r)$ $o 1 r r (r)$ $o 1 r r (r)$ $r r r (r)$ $N(s)$ $-1 1 1 r (r)$ $-1 1 r r r (r)$ $1 r s o (r)$ $r r s (1)$ $N(o)$ $1 o s r (r)$ $1 1 v o o (r)$ $r o r v (r)$ $O(IW)$ $N s s r (r)$ $r 1 s o o (r)$ $r v v v (r)$ $O(IW)$ $V r s r (r)$ $r 1 v v (r)$ $r 1 v v (r)$ $O(r W)$ $V r s r r (r)$ $r v v v v (r)$ $r v v v (r)$ $O(r W)$ $v r s r r (r)$ $r v v v v v v v v$	C(10)	۱٦٠٢(٤)	-1291(2)	٤٥٣٧(٣)	۳۸(۱)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	N(r)	۳۳۲ (۳)	-1989(8)	017V(7)	۳۹(۱)
$N(\bullet)$ $1 \circ \P Y(\P)$ $-1 \lor \circ \circ (\P)$ $\P \circ \Psi V(\P)$ $\xi \Lambda(1)$ $O(IW)$ $\Lambda \Psi \xi(\P)$ $\Upsilon 1 \Im \circ (\P)$ $-1 \lor \circ \Lambda(\P)$ $\circ \Im (1)$ $O(IW)$ $V \Psi \P(\P)$ $-1 \lor (\P)$ $-1 \lor \circ \Lambda(\P)$ $\circ \Im (1)$ $O(\Psi)$ $\nabla \Psi \P(\P)$ $-1 \lor (\P)$ $-1 \lor (\P)$ $\xi \Lambda(1)$ $O(\Psi)$ $\nabla \Psi \P(\P)$ $-1 \lor (\P)$ $-1 \lor (\P)$ $\xi \Lambda(1)$ $O(\Psi)$ $\Psi \xi(\P)$ $-1 \lor (\P)$ $-1 \lor (\P)$ $\xi \Lambda(1)$ $O(\Psi)$ $\Psi \xi(\P)$ $-1 \lor (\P)$ $-1 \lor (\P)$ $\Psi \Im \Psi (\Phi)$ $O(\xi W)$ $-1 \lor (\P \cap (\P)$ $V \lor 1 \Psi (\Lambda)$ $\xi \uparrow 0$ $V \lor (\Psi)$ $O(\xi W')$ $-1 \lor (\P \cap (\Psi)$ $0 \lor 1 \cdot (\Psi \cap (\Psi)$ $\nabla (\Psi)$ $V \lor (\Psi)$ $O(\xi W')$ $-1 \lor (\Psi \cap (\Psi)$ $0 \lor 1 \cdot (\Psi \cap (\Psi)$ $1 \lor (\Psi \cap (\Psi)$ $1 \lor (\Psi \cap (\Psi)$ $O(IS)$ $1 \lor (\Psi \cap (\Psi)$ $O(IS)$ $1 \lor (\Psi \cap (\Psi)$	N(t)	-1117(7)	-1974(1)	٦٦٤٥(٣)	٤٩(١)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	N(°)	1097(7)	_1400 (*)	۳٥٢٧(٣)	٤٨(١)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	O(IW)	٨٢٤(٣)	1170(7)	-1404(1)	٥٦(١)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	O(Y W)	۷۳۹(۳)	-147(7)	- ٢ ١ ٣٦(٢)	٤٨(١)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	O("W)	£ £ ₩ 1(₩)	- ۲ ۷ ۸ ٤ (٣)	111.(1)	££(1)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	O(\$W)	_Y00V(9)	۷۷٦٣(٨)	٤٦٥(٦)	٥٩(٢)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	O(* W')	-1+41(11)	7101(11)	077(V)	۷.(۲)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	O(\$W")	-11.(1.)	٥٧١٠(٢٠)	017(17)	۲۱(٤)
O(IS') 11AY(1Y) PTTP(1Y) AAY(4) 1YA(5)	O (IS)	۲۰۲(۱۳)	1795 (17)	£0£(V)	۱۳۳ (٤)
	O(IS')	1147(17)	WIWW(1Y)	۸۸۲(۹)	۱۲۸(٤)
$C(1S'') = \begin{bmatrix} yz \cdot (T \cdot) \\ yz \cdot (T \cdot) \end{bmatrix} = \begin{bmatrix} 1 \wedge 4 \cdot (T \cdot) \\ yz \cdot (T \cdot) \end{bmatrix} = \begin{bmatrix} TY \wedge (1T) \\ TY \wedge (1T) \end{bmatrix} = \begin{bmatrix} TY \wedge (1T) \\ TY \wedge (1T) \end{bmatrix}$	C(1S")	٧٤٠ (٣٠)	١٨٩٠(٣٠)	1	۳۷(٦)

	C(lS')	٦٠٤ (١١)	۲٤٧٣(۱۱)	1777(V)	۰.(۲)	
	C(lS)	11177(12)	1717 (17)	۱۳٦٣(٧)	۲ • (۳)	
'ah	la & Anisotron	ic displacement	narameters (Å	\mathbf{v} \mathbf{v} \mathbf{v} for the ti	itle complex [гı

Table \leq Anisotropic displacement parameters (Å' x \cdot) for the title complex. The anisotropic displacement factor exponent takes the form:

		-			-	
	U	U۲۲	U^{μ}	U۲۳	U۲	U ۲
Ga(l)	۲٦(۱)	۲۹(۱)	(۱) ۳۳	-۲(۱)	$\mathcal{V}(\mathcal{V})$	-۳ (۱)
N(l)	۲۹(۱)	۲٥(۱)	(۱)۳۲	-\$(1)	-1(1)	-Y(1)
0(1)	۲۹ (۱)	۳۸(۱)	۳۷(۱)	-٦(١)	۲(۱)	۲ (۱)
C(Y)	۲۸(۱)	(1)	۲۹(۱)	-0(1)	-٦(١)	-Y(1)
$O(\mathbf{t})$	۲٦(۱)	۲۹(۱)	۲۷ (۱)	-0(1)	-۲(۱)	-۳(۱)
C(٤)	۳۹(۲)	(۲) ۲۳	۲٤(١)	-٩(١)	۲(۱)	-1 \$(1)
$N(\mathbf{Y})$	۲٥(۱)	۳۱(۱)	۲.(۱)	-۲(۱)	-۳ (۱)	-0(1)
$O(\mathbf{Y})$	۲۸(۱)	۳۸(۱)	۲٦(۱)	·(1)	·(1)	(1)
C(Y)	۳٥(۲)	۲٥(۱)	۲٦(۱)	-٤(١)	-0(1)	-1.(1)
(۳) О	۳۲ (۱)	۲۹(۱)	۳٥(۱)	-Y(1)	-17(1)	-۲(۱)
C(°)	۳۱(۲)	٣٤(٢)	۲۹(۲)	-1.(1)	٤(١)	$-1 \cdot (1)$
(۲) О	۳۳(۱)	٤٠(١)	۲٦(۱)	-1(1)	-۳(۱)	-10(1)
C(\)	۲٦(۱)	۲۸ (۱)	۲۸(۱)	-٦(١)	(1)	-٦(١)
C(V)	۲۸(۲)	(۲) ۳۱	۳۰(۲)	-1(1)	(1)	-٤(١)
0(•)	117(3)	(۲) ۲۷	٤٣(٢)	-17(1)	-Y(Y)	-7 ٤ (٢)
C(1)	۲۹(۲)	(۱) ۳۳	۳۰(۲)	-V(1)	-0(1)	-٦(١)
O (V)	٦٣(٢)	۰.(۲)	٥٧(٢)	٤(١)	-9(1)	- " " ()
0 (^)	۳۸(۱)	۲۷(۱)	۳۹(۱)	-V(1)	-۲(۱)	-Y(1)
C(9)	۳۰(۲)	٤ • (٢)	۲۷(۲)	-0(1)	-Y(1)	-^(1)
$C(1 \cdot)$	۳۸(۲)	٦٢(٢)	۳٥(۲)	-7 5 (7)	-0(7)	-17(7)
C(11)	٣٤(٢)	۹۳(۳)	۲۹(۲)	-17(1)	۳(۱)	-17(1)
C(17)	۳۰(۲)	۲٦(۲)	۲٦(٢)	-٤(٢)	·(1)	-19(7)
C(17)	۲٥(۱)	۳۸(۲)	۲٥(۱)	۲(۱)	-Y(1)	-٦(١)
C(1£)	۳۷(۲)	۳۳(۲)	۳٦(٢)	۲(۱)	-1.(1)	-11(1)
C(^)	٤٤(٢)	٤٦(٢)	۲۹(۲)	-۳(۱)	-17(1)	-14(7)
C(19)	۳۱(۲)	۳٦(٢)	٥٣(٢)	-9(7)	-17(7)	-9(1)
C (1A)	۳۹(۲)	٤ ٤(٢)	٥٣(٢)	-V(Y)	-19(7)	-^(Y)
C(1V)	۳۱(۲)	۳۰(۲)	۲۳(۲)	-٦(٢)	-77(7)	-0(1)
C(17)	۳.(۲)	۲۹(۲)	٦١(٢)	-^(Y)	-1 2 (7)	-9(1)
C(10)	۳۱(۲)	۲۸(۲)	٥٣(٢)	-0(1)	-11(1)	-11(1)
N(Y)	۳۱(۱)	۲۷ (۱)	٥٢(٢)	-\$(1)	-17(1)	-0(1)
N(t)	۳۲(۲)	٥٣(٢)	٥٢(٢)	-17(7)	-17(1)	-٦(١)
N(•)	٣٤(٢)	£ Y(Y)	(۲) ٥٥	-۳(۲)	-17(1)	-9(1)
O(lW)	٥٨(٢)	٦٠(٢)	٤ • (١)	-٦(١)	-10(1)	-10(1)
O(Y W)	۳.(۱)	٥٢(٢)	٤١ (١)	-\$(1)	۳(۱)	-^(1)
O(* W)	٤٩(٢)	۳٥(١)	٤٢(١)	-17 (1)	-Y(1)	-Y(1)

 $- \mathbf{\tilde{\pi}} [h^{\mathbf{r}} a^{\mathbf{r}} U^{\mathbf{r}} + ... + \mathbf{\tilde{h}} h k a^{\mathbf{r}} b^{\mathbf{r}} U^{\mathbf{r}}]$

	x	У	z	U(eq)
H([£] C)	_~ ١٨٠	220.	٦٦£٩	۳۸
Н(۳С)	_ £ Y o 1	1۳	2190	٣٦
H(°C)	_^^^ 0	۳۹۸٦	٥٣٧٧	۳۹
$H(1 \cdot C)$	_ ~ ~ ~ ^	٥٣٢	_777	٥٣
H (¹)C)	- 4 • 4 9	۱۹۷۷	_1109	27
$H(\gamma C)$	_*17٣	3771	_ov.	07
H (\^C)	1890	_ 40 %	۷۳۷۵	٥٧
$H(\gamma VC)$	8088	_ £ Å • £	7518	٥١
$H(1^{C})$	8440	_#***	2708	٤٩
H("N)	_0 7 7	_17.7	£9.9	٥٨
H(YN [£])	_1 7 • A	_12.4	V777	٧٤
H(IN)	_1^^7	_1779	2402	٧٤
H(^Y N ^o)	2021	_*\\.	* 1 V T	۲ ۲
H(\N°)	V Y A	_1.77	3192	۲ ۲
H(^Y Wl)	9.7	2552	_1717	٨٤
H(IW)	222	۳۰۰۲	_****	٨٤
H(⁷ W ⁷)	1072	_0 9 A	_7 £ 7 £	۲ ۲
$H(^{\gamma}W^{\gamma})$	۳۸٦	_^ £ £	_* • ٧٦	۲ ۲
H(IW ^r)	5215	_~£~0	2201	11
H (⁷ W ⁷)	£ V 7 W	_*) \ Y	****	11

Table \circ Hydrogen coordinates (x \cdot , \cdot) and isotropic displacement parameters (Å' x \cdot , \cdot) for the title complex.

Table \checkmark Hydrogen bonds of the title compound (Å,°).

D-HA	(D-H)	(HA)	<(DHA)	(DA)	Α	
N°-Η ^γ N°	۰,۹۸۰	1,877	185,75	۲,۷۹۹(۵)	۰۳₩	
N°-H'N°	.,907	۲,٥	131,73	۲,97٧(٤)	۰۲W	[-x, -y, z]
Ν٤-Η٢Ν٤	۰,۷۸۷	۲,٥.٥	۱۷۳,۱۰	٣, ٢٨٨(٤)	۰۱S'	[-x, -y, z+1]
Νέ-ΗνΝέ	۰,۸۳۸	4,400	182,18	۲,۹۳۹(۵)	۰۳	
Ν"-Η"Ν	۰,۹۰۸	۱,۸۸۱	124,22	۲,۷۷٤(٤)	• ٣	
・) W-H ۲ W)	۰,۹۱۸	۱,۸۱۱	109,70	۲,٦٩٠(٤)	۰٤W'	[-x, -y+1, -z]
•) W-H ۲ W)	۰,۹۱۸	۲,۰٦٨	184,22	۲,۸۱۲(٤)	۰٤W	[-x, -y+1, -z]
・) W-H ۲ W)	۰,۹۱۸	2,129	130,89	۲,۹۰۹(٦)	۰ ۱ S	
・) W-H ۲ W)	۰,۹۱۸	2,328	129,92	٣,١٥٧(٥)	۰٤W'	[-x, -y+1, -z]
•) W-H) W)	۰,۹۳۷	1,823	۱۷۰,۳۰	۲,۷۷۱(٤)	• 1	[-x-1, -y+1, -z]
۰۳W-H۱W ۳	۰,۸۰۹	۲,.٦٧	138,08	2,102(2)	• ^	[x+1, y-1, z]
۰۳ ₩-Η ۲₩۳	۰,۷۸۸	1,997	177,77	۲,۷٥٥(٥)	. 0	[x+1, y, z]
۲ W-H ۲ W ۲	۰,۸۳٥	1,900	175,47	۲,۷۸۷(٤)	• £	[-x, -y, -z]
$\cdot \mathbf{W} - \mathbf{H} \mathbf{W}$	۰,۸۸۹	۲,۳۱۰	110,70	۲,۸۱۳(۰)	·1S	[-x, -y, -z]

References

[1] Zafar, A., Geib, S. J., Hamuro, Y., Carr, A. J., Hamilton, A. D., "Hydrogen bonding control of molecular self-assembly: aggregation behavior of acylaminopyridine-carboxylic acid derivatives in solution and the solid state", Tetrahedron \bullet , $(\checkmark \cdots) \land \bigstar \checkmark \land \land \checkmark \lor$.

[*] Schmuck, C., "Highly stable self-association of \bullet -(guanidiniocarbonyl)-¹H-pyrrole-^{*}-carboxylate in DMSO - the importance of electrostatic interactions", Eur. J. Org. Chem. (1999) YT9V-Yt. T.

[Υ] Moghimi, A., Ranjbar, M., Aghabozorg, H., Jalali, F., Shamsipur, M., Yap, G.P.A., Rahbarnoohi, H. A., "novel pyridine containing self-assembling system: synthesis, characterization, X-ray crystal structure, "C solid phase NMR and solution studies", J. Mol. Struct. $\Im \circ$, $(\Upsilon \circ \Upsilon)$ $\Im \Upsilon - \Im 4$.

[•] Ranjbar, M., Taghavipur, M., Aghabozorg, H., Moghimi, A., Jalali, F., Shamsipur, M., "Synthesis, X-ray crystal structure and solution studies of Cu(II) complexes of a Pyridine containing self-assembling system", Polish J. Chem., $\forall \forall, (\forall \cdot \cdot \forall) \forall \land \bullet - \forall \forall t$.

[1] Ranjbar, M., Moghimi, A., Aghabozorg, H., Yap, G.P.A., "Crystal structure of zinc(II) complex of a pyridine containing self- assembling system", Anal. Sci., 1^{1} , $(1 \cdot \cdot 1)^{1}$, 1^{1} .

[\forall] Moghimi, A., Ranjbar, M., Aghabozorg, H., Jalali, F., Shamsipur, M., Chadah, R.K., "Synthesis, NMR characterization, X-ray crystal structure and solution studies of Ni(II) complexes of a pyridine containing self-assembling system", J. Chem. Research(S), ($\forall \cdot \cdot \forall$) $\forall \forall \forall \cdot \xi \forall \vartheta$.

[\land] Moghimi, A., Ranjbar, M., Aghabozorg, H., Jalali, F., Shamsipur, M., Chadha, K.K., "Synthesis, characterization, and X-ray crystal structure of Co(II) and La(III) complexes of a pyridine containing self-assembling system and solution studies of the Co(II) complex", Can. J. Chem. $\land \cdot$, $(\uparrow \cdot \cdot \uparrow)$ 17 $\land \lor$ -17 $\land \uparrow$.

[**1**] Ranjbar, M., Aghabozorg, H., Moghimi, A., "Crystal structure of bis (*Y*, *T*-diaminopyridinium) diaqua-bis-(*Y*, *T*-pyridinedicarboxylato)- bis(*Y*, *T*-pyridinedicarboxylato)-dibismuthate(III)tetrahydrate, (C₁, H₁, O₁, N_tBi_t) (C₂H₄N_t)_t · tH₁O, Z.Kristallogr", NCS Y1A (Y · · Y) tY - tY t.

[1.] Moghimi, A., Shokrillahi, A., Shamsipur, M., Aghabozorg, H., Ranjbar, M., X-ray crystal structure and solution studies of

"hexacoordinated mercury(II) complex of a pyridine containing proton transfer compound", J. Mol. Struct. $\vee \cdot \vee (\uparrow \cdot \cdot \pounds)$ $\pounds 9-07$.

[1] Ranjbar, M., Moghimi, A., Aghabozorg, H., "Crystal structure of a binuclear seven-coordinate tin(IV) complex", Anal. Sci. 14, (1.14, 1.14) x^V.

[14] Ranjbar, M., Aghabozorg, H., Moghimi, A., Yanovsky, A., "Crystal structure of Bi(III) complex of a pyridine containing self-assembling system", Anal. Sci. 14, ($\tau \cdot \cdot 1$) $1 \leq \tau q - 1 \leq V \cdot .$

[$\$ "] Ranjbar, M., Aghabozorg, H., Moghimi, A., "A seven-coordinate pyridine- $\$ "."-dicarboxylate-bridged cadmium(II) complex, at $\$ ". Acta Cryst. E $\$ ($\$ ".") m"."- $\$ "."

[12] Ranjbar, M., Aghabozorg, H., Moghimi, A., "Crystal structure of a binuclear polymeric self-assembled lead(II) complex", Anal. Sci. 19 $(1 \cdot \cdot \cdot)$ $\wedge \cdot \cdot \cdot \cdot \cdot$