

Preparation and Theoretical Study of some Transition Metal Complexes with Acetylenic Amine and Study of its Biological Activity

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Abstract

Twelve new complexes were synthesized and characterized by reaction salts of with (Cr^{+5} , Mo^{+3} and W^{+6}) with bidentate ligands (acetylenic amine), these:

$L1 = (N,N\text{-Dimethyl Propargyl amine})$, $L2 = (N,N\text{- Propargyl Piperidine})$,

$L3 = (N,N\text{- Propargyl Morpholine})$, $L4 = (N,N\text{- Methyl -N- Propargyl benzyl amine})$.

Studying of complexes by using suitable methods have been diagnosed in Uv-Visible, IR, Magnetic susceptibility, atomic absorption, electric conductivity measurement, all result obtained from different techniques above which were found that their corresponding with the proposed structures for the prepared complexes has octahedral structure. A theoretical treatment of the formation of complexes was studied, this was done using the HYPERCHEM-6 program for the Molecular mechanics and Semi-empirical calculations. The free ligand and its complexes have been tested for their antibacterial activities against Two type of human pathogenic bacteria: (*Staphylococcus aureus*), (*Escherichia coli*). the first group are Gram positive while the second group are Gram negative (by using agar well diffusion method). Finally, it was found that compounds show different activity of inhibition on growth of the bacteria.

1. Introduction

Acetylenic amines are important class of compounds for their pharmacological properties such as activity, low toxicity and easy absorption from the body. moreover these compounds are electron rich and easy to bond with receptor proteins⁽¹⁾. Some of their pharmaceutical uses as anticancer⁽²⁾ and hypertensive agent⁽³⁾.

In investigating the importance of acetylenic bond for pharmacological activity it was through possible that the electron rich acetylenic bond attaches itself to the positive binding site in the cholinergic receptor, in which case its presence is probably necessary for the effect. it is also possible that the rigidity of the system serves the purpose of keeping the two nitrogen atoms at suitable distance from each other.

The acetylenic amines derived from piperazine having two acetylenic functions are expected to have similar anticholinergic effect and may be used to treat Parkinson disease. The first stable acetylenic complexes were reported by Gelman⁽⁴⁾ who showed that the acetylenic glycol. Forms complexes $\text{trans-}[\text{PtCl}_2(\text{ac})\text{Py}]$ analogous to $\text{trans-}[\text{PtCl}_2(\text{C}_2\text{H}_4)\text{Py}]$ ⁽⁵⁾. Later work⁽⁶⁾ showed that olifine complexes of the types $\text{K}[\text{PtCl}_3(\text{ac})]$. Alkyne Pt^{+2} complexes⁽⁷⁾ of the chloro bridge type $[\text{Pt}_2\text{Cl}_4(\text{ac})]$ and $\text{M}[\text{Pt}_2\text{Cl}_3(\text{ac})]$ ($\text{M}=\text{Na}, \text{K}$).

A large number of compounds have been prepared specially those having aromatic rings substitute in 1,4-positions to have crystals with rigid and linear structures. In addition a number of compounds with piperazine ring⁽⁸⁾ and acetylenic group⁽⁹⁾ were prepared and found to liquid crystalline properties^(10,11). The wide range of application of the ligand and its metal complexes aroused our interest to prepare some of these metal complexes.

2. Experimental

2.1 Instrumentation

IR spectra were recorded on a PYE-UNICAM SP3-100 as KBr disc. UV-VIS data were recorded on a HITACHI-U-2000 and Melting point determined by Gallen Kamp. Electrical conductance was measured at ($10^{-3}\text{-}10^{-4}$)M on conductivity CDC304 (JENWEY 4070). Elemental analysis were done by Atomic absorption AA-680G Shimadzu, Polarizing Microscope Labrotux (2-po) Letizand Camera Orthomato 25 Letiz, Magnetic susceptibility B.M6 Bruker.

2.2 Material

All the chemical used were of analar grade, and purchased from Sigma-Aldrich. Metal salts were purchased from Fluka AG Buchs. All the solvents used were of spectroscopic grade.

2.3 Preparation of the ligand

A- L1= (N,N-Dimethyl Propargyl amine) , L2= (N,N- Propargyl Piperidine) , were prepared according to the literature⁽⁵⁾

B- L3= (N,N- Propargyl Morpholine) , L4= (N,N- Methyl -N- Propargyl benzyl amine) , were prepared according to the method⁽⁶⁾. the ligands are listed in table(1).

2.4 General Procedure for Preparation of Complexes

All of complexes were prepared by the following methods; A solution of the ligand (2 mmole/l) in absolute ethanol were prepared and reacted with various metal chlorides in the required molar ratio. To a solution of (L) (2 mmole/l) in absolute ethanol ,a hot ethanolic solution (96%) containing (1 mmole/l) of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was gradually added with stirring the product .the color of the resultant mixture changed immediately , the mixture was left over night . a colored solid precipitate was separated and collected by filtration under vacuo, then it was washed successively with ethanol and recrystallized from absolute ethanol/ether to give colored complexes . Analogous complexes were prepared in a similar manner to that described above by adding a hot solution of metal chloride ($\text{MoCl}_5 \cdot 6\text{H}_2\text{O}$ or $\text{WCl}_6 \cdot 6\text{H}_2\text{O}$) (1 mmole/l) to a solution of ligand (2 mmole/l) . the complexes are listed in table(2).

2.5- Study of biological activity for ligands and their metal complexes

The biological activity of the ligands and their metal complexes were studied against two selected type of bacteria which included *Escherichia coli* as gram negative (-Ve) and *Staphylococcus aureus* as gram positive (+Ve) to be cultivated and as control for the disc sensitivity test⁽⁹⁾ , this method involves the exposure of the zone of inhibition toward the diffusion of micro-organism on agar plate. The plates were incubated for (24 hours) , at 37°C , the zone of inhibition of bacteria growth around the disc was observed.

3. RESULT AND DISCUSSION

3.1 IR Spectra

The spectra of all prepared complexes were prepared with ligand spectra in the region $(4000-200) \text{ cm}^{-1}$. stretching vibration of $(\text{C}\equiv\text{C})$ bonds for the prepared ligand appear near $(2100) \text{ cm}^{-1}$ ⁽¹³⁾. This peak will shifted to lower frequency by $(490) \text{ cm}^{-1}$ (i.e. to $1750-1650) \text{ cm}^{-1}$ the peak which belong to the frequency $(\text{C}\equiv\text{C})$ disappeared producing the change in ligand peak shape and appear intensity more than complex as shown in table(1). $\nu^{\text{M-N}}$ frequency appears in the region $(315-345) \text{ cm}^{-1}$ which indicating the involving of nitrogen atoms in coordination with metallic ion. In addition, new bands appears attributed to the M-Cl stretching vibration table(2).

3.2. Electronic Spectra

UV-Visible spectra for the prepared ligand show two bands, the first band at (319) nm and the second at (372) nm as shown in table (1). comparing the UV-Vis for free ligand solution with metal complexes ,clear sudden change have been made in bands spots whether increasing or decreasing in wavelength or by new absorbance band for all preparation complex which belong coordination complex formation ,the change in color we occurred after mix ligands solution with metal salt, the mixtures color differ free ligand and metal salt colors indicate occurring complexation , the data in table (2) clearly show that that bands in all complexes appear shifted in λ_{max} , compared to the same bands in the free ligand signs this band is due to $(\pi-\pi^*)$ and $(n-\pi^*)$ and this shifted in λ_{max} can be to indicate the complexation between ligand and metal ions⁽¹⁴⁾.

3.3. Magnetic Study

From table(2) the magnetic susceptibility were experimentally measured for $(\text{Cr}^{+3}$, Mo^{+5} and W^{+6}) complexes were correspondences with theoretical data for its complexes (coordination number six) with octahedral structure⁽¹⁵⁾.

3.4. Molar Conductance

The measurements of the molar electrical conductivity of the complexes in DMSO solvent are prepared in table (2). The results clearly show the high values for the molar conductivity of the complexes of metal ions are electrolyte.

3.5. Stoichiometric Study

Molar ratio (1:2) ligand to metal (ML_2) was also obtained for the complexes by molar-ratio method as shown in fig.(1).

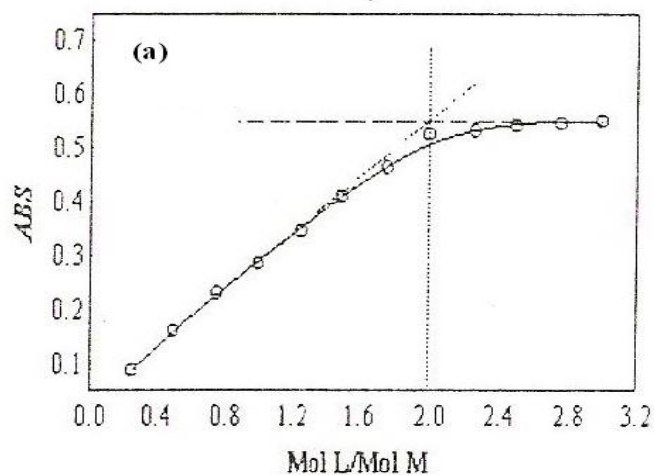


Fig. (1): Molar-ratio curve for $[\text{Cr}(\text{L}_1)_2\text{Cl}_2]\text{Cl}$ of prepared complexes

3.6 The proposed structure

According to the results obtained from ir, uv/vis, molar ratio, molar conductivity and atomic absorption measurements for the prepared complexes, the proposed molecular structure of the complexes has an octahedral structure as shown below fig. (2) .

Fig.(2): The proposed structure of $[\text{M}(\text{L}_4)_2\text{Cl}_2]\text{Cl}_x$ complexes where $\text{M} = \text{Cr}(\text{III}), \text{Mo}(\text{V})$ and $\text{W}(\text{VI})$.

3.7 Theoretical Study:

The ball and cylinders and some of selected structural parameters (bond length and angles) of the optimized geometries are shown in fig.(3) table (3).

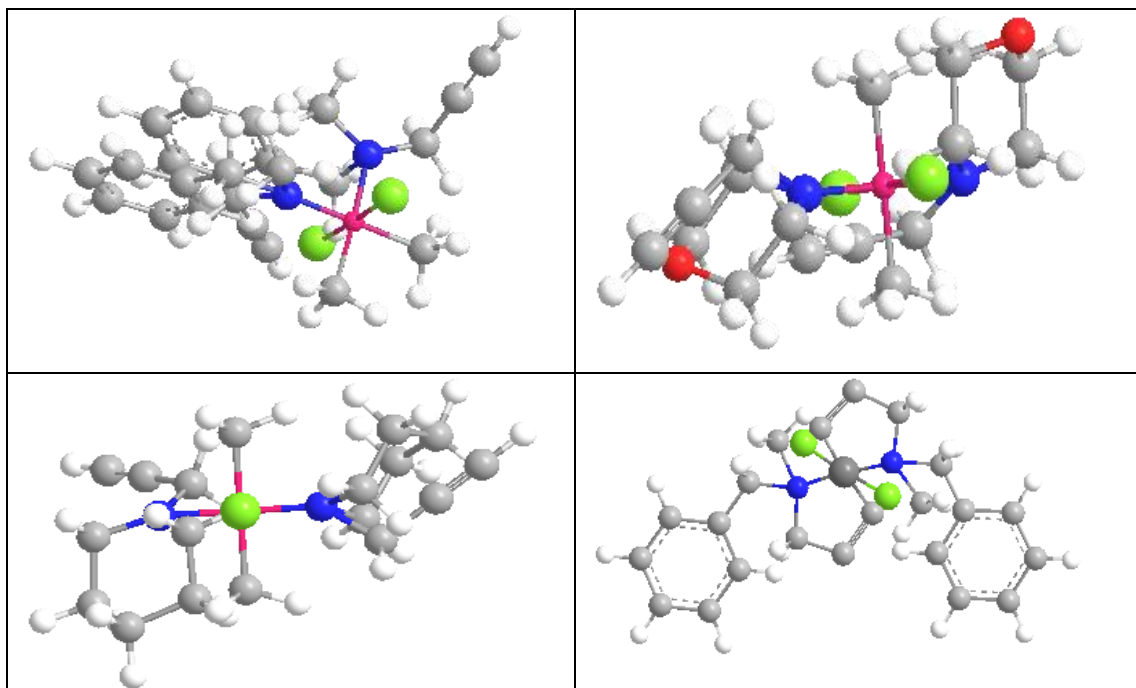
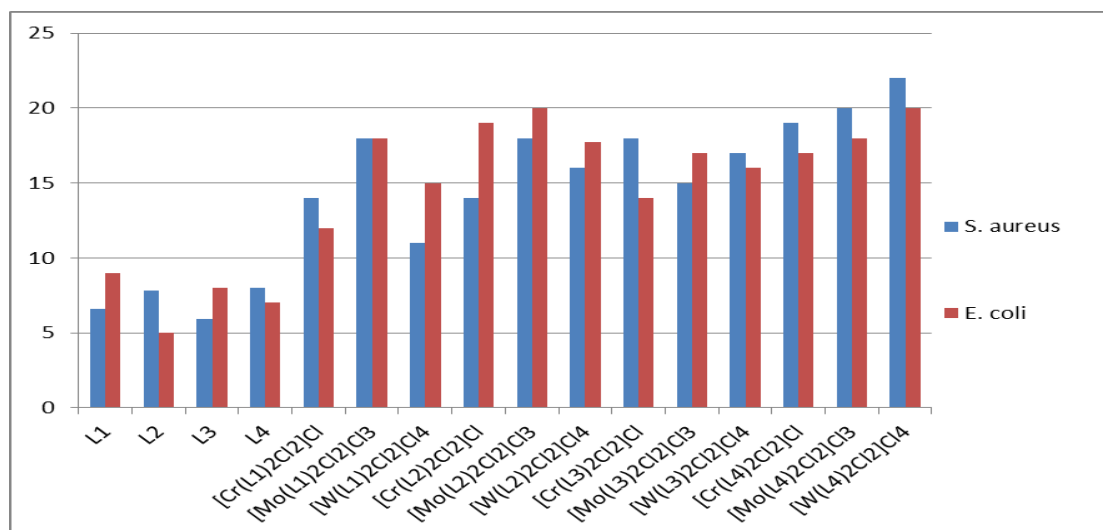


Fig.(3): The optimized structural geometry of $\text{Cr}(\text{III}), \text{Mo}(\text{V})$ and $\text{W}(\text{VI})$ complexes

As shown in this figure, there is no obvious trend for the variation of these parameters. The values of the bond length and angles of the optimized geometries are quite similar to the experimental results of the corresponding compounds.

3.8 Biological Activity:

Antibacterial activity of the ligands and its complexes was tested on Gram positive bacteria, *Staphylococcus aureus* and Gram negative, *E. coli*, using nutrient agar medium by the well diffusion method⁽¹⁶⁾. The antibacterial activities of the samples was evaluated by measuring the inhibition zone observed around the tested materials fig.(4). The values indicate that all metal complexes have higher activity than the free ligands. Such increase activity of the metal chelates can be explained on the basis of chelation theory⁽¹⁷⁾.



Fig(4): The effect of ligands and their metal complexes toward bacteria

Table(1): physical properties of the ligands (L₁, L₂, L₃).

No.	Name and structure of compound	Yield %	colour	M.P °C picrate	Elemental analysis cal. (%found) %			IR spectra cm ⁻¹	Uv-Vis. nm
					C	H	N		
L ₁	N,N-dimethyl Propargyl Amine	82	Pale yellow	109-111	75.62 (75.60)	11.79 (11.76)	12.60 (12.55)	ν(≡CH)3300, ν(C≡CH)2100, ν(CH)2950	311,382 In DMSO
L ₂	N-Propargyl Piperidine	70	Pale yellow	145-146	77.99 (77.98)	10.46 (10.42)	11.37 (11.34)	ν(≡CH)3300, ν(C≡CH)2100, ν(CH)2968	308,389 In DMSO
L ₃	N-Propargyl Morpholine	90	Pale yellow	119-122	67.17 (67.12)	8.86 (8.83)	11.19 (11.17)	ν(≡CH)3310, ν(C≡CH)2110, ν(CH)2960	314,386 In DMSO
L ₄	N-benzyl-N-methyl prop-2-yn-1-amine	84	Pale yellow	100-102	82.97 (82.94)	8.23 (8.21)	8.80 (8.75)	ν(≡CH)3310, ν(C≡CH)2100, ν(CH)2978	302,372 In DMSO

Table(2): Physical characterization ,analytical and Molar Conductance data of the compounds

Compound	Yield %	Colour	$\Delta M/S$ cm^2 mol^{-1}	M.P C°	UV/VIS nm	μ_{eff} (BM)	Elemental analysis (% found) % cal		IR spectra cm^{-1}
							Cl	M	
$[Cr(L_1)_2Cl_2]Cl$	80	Dark green	85	160-162	309,382, 615	3.7	(27.95) 27.96	(13.63) 13.65	$\nu^{(C=C)}$ 1680 _(s) , $\nu^{(M-N)}$ 295 _(m) , $\nu^{(M-Cl)}$ 340 _(w)
$[Mo(L_1)_2Cl_2]Cl_3$	80	blue	95	192-194	295,374, 461	-	(35.75) 35.79	(19.35) 19.36	$\nu^{(C=C)}$ 1705 _(s) , $\nu^{(M-N)}$ 315 _(s) , $\nu^{(M-Cl)}$ 335 _(w)
$[W(L_1)_2Cl_2]Cl_4$	60	Yellow	110	210-212	297,382, 424	-	(34.35) 34.39	(29.68) 29.70	$\nu^{(C=C)}$ 1695 _(s) , $\nu^{(M-N)}$ 270 _(m) , $\nu^{(M-Cl)}$ 345 _(w)
$[Cr(L_2)_2Cl_2]Cl$	70	Dark green	65	165-167	319,380, 635	3.74	(26.26) 26.30	(12.81) 12.84	$\nu^{(C=C)}$ 1740 _(s) , $\nu^{(M-N)}$ 318 _(s) , $\nu^{(M-Cl)}$ 338 _(w)
$[Mo(L_2)_2Cl_2]Cl_3$	40	blue	75	195-197	300,333, 495	-	(34.11) 34.14	(22.84) 22.86	$\nu^{(C=C)}$ 1695 _(s) , $\nu^{(M-N)}$ 260 _(w) , $\nu^{(M-Cl)}$ 325 _(m)
$[W(L_2)_2Cl_2]Cl_4$	85	Yellow	100	203-205	297,370, 475	-	(33.08) 33.10	(28.56) 28.59	$\nu^{(C=C)}$ 1710 _(s) , $\nu^{(M-N)}$ 290 _(w) , $\nu^{(M-Cl)}$ 3500 _(s)
$[Cr(L_3)_2Cl_2]Cl$	75	Dark green	60	173-175	306,387, 630	3.71	(26.00) 26.04	(12.69) 12.71	$\nu^{(C=C)}$ 1675 _(s) , $\nu^{(M-N)}$ 290 _(m) , $\nu^{(M-Cl)}$ 398 _(w)
$[Mo(L_3)_2Cl_2]Cl_3$	70	blue	70	187-189	299,339, 415	-	(33.85) 33.88	(18.29) 18.32	$\nu^{(C=C)}$ 1685 _(s) , $\nu^{(M-N)}$ 305 _(s) , $\nu^{(M-Cl)}$ 405 _(w)
$[W(L_3)_2Cl_2]Cl_4$	65	Yellow	80	195-197	286,377, 388	-	(32.88) 32.90	(28.39)2 8.42	$\nu^{(C=C)}$ 1690 _(s) , $\nu^{(M-N)}$ 275 _(m) , $\nu^{(M-Cl)}$ 395 _(w)
$[Cr(L_4)_2Cl_2]Cl$	65	Dark green	70	158-160	310,383, 625	3.77	(22.29)2 2.32	(10.87)1 0.90	$\nu^{(C=C)}$ 1680 _(s) , $\nu^{(M-N)}$ 328 _(s) , $\nu^{(M-Cl)}$ 410 _(w)
$[Mo(L_4)_2Cl_2]Cl_3$	70	blue	85	175-177	300,382, 445	-	(28.86)2 9.98	(16.18)1 6.21	$\nu^{(C=C)}$ 1690 _(s) , $\nu^{(M-N)}$ 280 _(w) , $\nu^{(M-Cl)}$ 415 _(m)
$[W(L_4)_2Cl_2]Cl_4$	55	Yellow	90	215-217	296,372, 440	-	(29.75)2 9.77	(25.68)2 5.71	$\nu^{(C=C)}$ 1685 _(s) , $\nu^{(M-N)}$ 295 _(w) , $\nu^{(M-Cl)}$ 400 _(s)

Table (3) : structural parameters, bond length (°A) and angles(°) of the studied Molecules.

Parameter										
Bond lengths (°A)										
C(29)-H(61)	1.1000	C(17)-H(51)	1.1130	1.1130	C(10)-H(41)	1.0900	1.0900	C(29)-C(24)	1.3370	1.4200
C(16)-C(24)	1.4970	1.4970	C(18)-C(19)	1.3370	1.4200	N(2)-C(17)	1.4380	1.4380	N(7)-C(16)	1.4380
Du(11)-Cl(15)	1.9900	Du(11)-Cl(14)	1.9900	1.9900	N(2)-Du(11)	1.6760	1.6760	N(7)-Du(11)	1.6760	
C(13)-Du(11)	1.7700	C(12)-Du(11)	1.7700	1.7700	N(7)-C(8)	1.4380	1.4380	C(6)-N(7)	1.4380	1.4380
N(2)-C(3)	1.4380	1.4380	N(2)-C(1)	1.4380	1.4380	H(61)-C(29)-C(24)	120.0000	120.0000		
C(24)-C(29)-C(28)	120.0000	1.4200	1.4200	C(29)-C(24)-C(16)	120.0000	121.4000	C(22)-C(21)-C(20)	120.0000	1.4200	
C(21)-C(20)-C(19)	120.0000	1.2600	1.2600	C(20)-C(19)-C(18)	120.0000	1.5030	C(23)-C(18)-C(17)	120.0000	121.4000	
H(51)-C(17)-H(50)	109.5200	109.4000	109.4000	H(51)-C(17)-C(18)	109.4620	109.4100	H(51)-C(17)-N(2)	109.4620	1.4200	
H(50)-C(17)-N(2)	109.4420	1.4200	1.4200	C(18)-C(17)-N(2)	109.5000	1.4200	H(49)-C(16)-N(7)	109.4620	1.4200	
H(48)-C(16)-N(7)	109.4420	1.4200	1.4200	C(24)-C(16)-N(7)	109.5000	1.4200	H(47)-C(13)-Du(11)	109.4620	1.4200	
H(46)-C(13)-Du(11)	109.4420	1.4200	1.4200	H(45)-C(13)-Du(11)	109.5000	1.4200	H(44)-C(12)-Du(11)	109.4620	1.4200	
H(43)-C(12)-Du(11)	109.4420	1.4200	1.4200	H(42)-C(12)-Du(11)	109.5000	1.4200	Cl(15)-Du(11)-Cl(14)	177.2240	1.4200	
Cl(15)-Du(11)-N(2)	89.8528	1.4200	1.4200	Cl(15)-Du(11)-N(7)	87.2239	1.4200	Cl(15)-Du(11)-C(13)	92.7722	1.4200	
90.1472										
Cl(14)-Du(11)-N(2)	90.0000	90.0000	90.0000	Cl(14)-Du(11)-N(7)	90.0000	90.0000	Cl(14)-Du(11)-C(13)	90.0000	90.0000	90.0000
N(2)-Du(11)-N(7)	86.9600	86.9600	86.9600	N(2)-Du(11)-C(13)	90.0000	90.0000	N(2)-Du(11)-C(12)	180.0000	180.0000	N(7)-Du(11)-C(13)
N(7)-Du(11)-C(12)	93.0400	93.0400	93.0400	C(13)-Du(11)-C(12)	90.0000	90.0000	H(39)-C(8)-N(7)	109.4420	109.5000	109.5000
C(16)-N(7)-Du(11)	76.1677	76.1677	76.1677	C(16)-N(7)-C(8)	101.3470	101.3470	C(16)-N(7)-C(6)	92.4261	92.4261	Du(11)-N(7)-C(8)
C(8)-N(7)-C(6)	120.0000	120.0000	120.0000	H(38)-C(6)-N(7)	109.4620	109.4620				
Bond angles(°)										
N(2)-C(17)	1.4380	1.4380	Du(11)-Cl(15)	1.9900	Du(11)-Cl(14)	1.9900	N(2)-Du(11)	1.6760	N(7)-Du(11)	1.6760
C(13)-Du(11)	1.7700	1.7700	C(12)-Du(11)	1.7700	N(7)-C(8)	1.4380	1.4380	C(6)-N(7)	1.4380	1.4380
1.4380	1.4380	1.4380	N(2)-C(1)	1.4380	H(51)-C(17)-N(2)	109.4620	1.4200	H(50)-C(17)-N(2)	109.4420	1.4200
C(18)-C(17)-N(2)	109.5000	109.5000	C(13)-Du(11)-C(12)	90.0000	90.0000	H(40)-C(8)-N(7)	109.4620	H(39)-C(8)-N(7)	109.4420	109.4420
C(9)-C(8)-N(7)	109.5000	109.5000	C(16)-N(7)-Du(11)	76.1677	76.1677	C(16)-N(7)-C(8)	101.3470	Du(11)-N(7)-C(8)	120.0000	120.0000
Du(11)-N(7)-C(6)	120.0000	120.0000	H(38)-C(6)-N(7)	109.4620	109.4620	H(37)-C(6)-N(7)	109.4420	H(36)-C(6)-N(7)	109.5000	109.5000
H(34)-C(3)-N(2)	109.4620	109.4620	124.3000	H(33)-C(3)-N(2)	109.4420	120.0000	120.0000	C(4)-C(3)-N(2)	109.5000	120.0000
C(17)-N(2)-Du(11)	177.1540	177.1540	120.0000	C(17)-N(2)-C(3)	57.1535	120.0000	120.0000	Du(11)-N(2)-C(3)	120.0000	120.0000
Du(11)-N(2)-C(1)	120.0000	120.0000	120.0000	C(3)-N(2)-C(1)	120.0000	120.0000	120.0000	H(32)-C(1)-N(2)	109.4620	120.0000
H(31)-C(1)-N(2)	109.4420	109.4420	120.0000	H(30)-C(1)-N(2)	109.5000	120.0000	120.0000			

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