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Synthesis and Crystal Structures of Some New Metal(II) Complexes with NNO Functionalized Ligands

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Abstract: Complexes of the general formula [ML_2] [M = Ni, Zn, Cu; L = 2-pyridinecarbaldehyde benzoylhydrazone (HPBH, **3a**), 2-pyridinecarbaldehyde isonicotinoylhydrazone (HPIH, **3b**), 2-pyridinecarbaldehyde 2'-thienoylhydrazone (HPTH, **3c**)] were synthesized by reaction of metal-acetate in boiling methanol with the ligands **3a-c** in 2:1 ligand to metal mole ratio. X-ray crystallographic investigation of the three complexes $(PBH)_2Ni$ **(4a)**, $(PIH)_2Ni$ **(4b)** and $(PIH)_2Zn$ **(6b)** is reported. All three compounds crystallize in the triclinic space group $P\bar{1}$ and Z = 2 at 173 K with a = 11.374(9)Å, b = 11.596(7)Å, c = 11.727(7)Å, α = 105.60(4)° , β = 104.30(5)°, γ = 104.98(6)° for $(PBH)_2Ni$ **(4a)**; for $(PIH)_2Ni$ **(4b),** a = 11.188(9)Å, b =11.445(7)Å, c = 12.004(7)Å, α = 107.04(4)°, β = 103.44(5)°, γ = 105.11(6)° and for $(PIH)_2Zn$ **(6b),** a = 11.222(9)Å, b = 11.501(7)Å, c = 12.045(7)Å, α = 106.63(4)°, β = 102.92(5)°, γ = 106.09(6)°. The metal centers in these complexes are surrounded by two ligand molecules in a meridional, slightly distorted octahedral manner.

Key words: Investigation of metal(II) complexes, Schiff bases, N, N, O tridentate ligands.

تحضير معقدات لبعض المعادن ذات اتصال من خلال ذرات (NNO) وعرض شكل أشعة إكس لها

ملخص: تم في هذا البحث تحضير معقدات ذات صيغة (ML_2) لمعادن النيكل والزنك والنحاسمع بنزويل هيدرازونات ألدهيدات البيردين والأيزونيكوتين والثيوفين، وذلك بتفاعل خلات المعدن مع الهيدرازونات المعينة بنسبة 1:2 . وقد تم تحديد أشكال المركبات منخلال عمل أشعة إكس لبعض بلوراتها، وقد كان الشكل الهندسي حول المعدن قريبا من الشكل ثماني الأوجه.

Introduction:

Schiff base ligands have been widely used in the field of coordination chemistry [1]. Their complexes have been used in catalytic reactions [2], industrial processes [3,4] and as models for biological systems [5,6].

The metal-hydrazone complexes continue to attract considerable attention owing to their potential applications in industry, non-linear optics [7], and interesting biological activities [8]. They act in processes such as antibacterial, antitumoral, antiviral, antimicrobial and antituberculosis [9].

Newly prepared, aroylhydrazone manganese(II) complexes are highly selective catalysts for oxidation of cyclohexene into its epoxide which is one of the most useful synthetic intermediates for the preparation of oxygen-containing natural products or the production of epoxy resins [10].

Quite recently, some new metal(II) complexes, $M(II)L_2$ [M = Mn, Co, Ni, Cu and Zn] of 2-acetylpyridinebenzoylhydrazone ligands containing the trifunctional N, N, O-donor system have been synthesized, and two of them were crystallographically characterized [11].

Selected first-row transition metal complexes with 2-pyridinecarbaldehyde isonicotinoylhydrazone (**3b**) and 2-pyridinecarbaldehyde (4'-aminobenzaldehydehydrazone) (**3d**) were recently synthesized by Bernhardt et al in an attempt to design and synthesis of ligands that exhibit high Fe chelation efficacy. It was found that, divalent first-row transition metals (Mn, Fe, Co, Ni, Cu and Zn) readily form bis (complexes) with the above ligands with each ligand coordinated meridionally through its pyridine-N, imine-N and carbonyl-O atoms, forming distorted octahedral cis-MN_4O_2 complexes.

The isonicotinoyl ring N-atom was found to be an effective ligand with some metals (Mn, Co and Zn) leading to complexes other than the simple divalent ML_2 complexes.

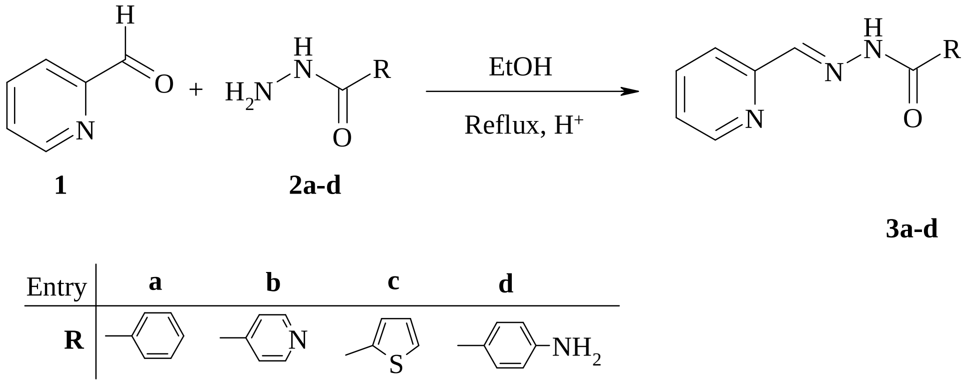
Divalent ZnL_2 and polymeric $ZnLSO_4$ complexes were obtained from reaction of **3b** with $ZnCl_2$ and $ZnSO_4.7H_2O$, respectively.

The present work will investigate the reaction of metal acetates (M = Ni, Cu and Zn) with different ligands derived from condensation of acid hydrazides **2** with pyridine 2-carbaldehyde**1**.

The effect of the R-group in the course of complexation will be investigated

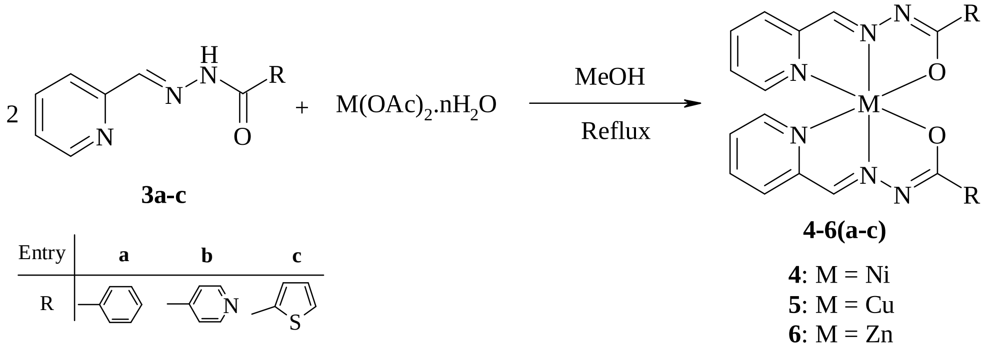
Results and Discussion

The Schiff base ligands (**3a**,**b**) [12] and (**3c**) [13] used in this work were synthesized by condensation of acid hydrazides (**2a-c**) with pyridine-2-carbaldehyde (**1**) in 1:1 mole ratio in ethanol. (Scheme 1).



Scheme 1

The metallation of these ligands with metal(II) acetate [metal(II) = Ni(II), Cu(II) and Zn(II)] in 2:1 ligand to metal mole ratio yielded six coordinate complexes **4-6**, in which the schiff base ligands act as N, N, O tridentate ligands forming stable 5-membered rings by binding with the pyridine-N, the imine-N, and the amide-O atoms (Scheme 2).



Scheme 2

Conductivity measurements:

Molar conductance of the complexes determined in $CHCl_3$ solution are almost negligible, indicating that the complexes are electrically non conductive [14].This suggests that the whole complex is neutral with two uninegative ligands.

IR spectra:

The IR spectra of the ligands has several prominent bands appearing at 3470 and 1659 cm^{-1} due to N-H and C=O stretching modes, respectively. Both these bands disappeared on complexation and a new C-O band at 1064-1078 cm^{-1} appeared.

Mass spectrometry:

The mass spectra of complexes show a peak due to the ligand plus proton ion and the molecular ion peak of the complex, which is in consistence with the proposed structure and it also ensures that each ligand lost one proton upon complexation.

NMR spectra:

^{1}H NMR spectra for the complexes of Ni(II) and Cu(II) were not helpful for identification due to their paramagnetism.

^{1}H NMR spectra of the zinc complexes ***(6a,b***) gave some information about these compounds, but, no peak was detected for the (NH) proton in these complexes. Some changes in the aromatic region and its chemical shift can be observed, but the complexity of the signals does not allow to interpret this in detail. The chemical shift observed for the (CH=N) proton about 8.5 ppm is an evidence for involvement of the nitrogen in coordination to the central zinc ion. The ^{13}C NMR of **6b** show the correct number of signals (10) in accordance with the suggested structure.

Electronic spectra:

Absorption spectra were obtained in methanol and the resulting data are given in the Experimental section. A strong band in the range 364-378 nm, and two or more moderately intense bands in the range 233-297nm are observed. The intense band near 370 nm may be associated with a charge transfer transition [15]. The last bands below 297 nm are also observed in the free ligand (209-318 nm) and hence can be attributed to intraligand transition bands.

Description of the crystal structures

The three compounds that have been crystallographically investigated are isostructural. In addition, they all have one H_2O and one $CHCl_3$ molecule in the asymmetric unit.

The structure of ***(4a)*** consists of two tridentate ligands coordinating the central nickel(II) ion such that the deprotonated spanning ligands produce a neutral nickel(II) complex containing a NiN_4O_2 meridionally coordination sphere. Each of the two ligands provide the pyridine-N, the imine-N and the amide-O as the metal coordinating atoms and form two five membered chelate rings upon chelation with the nickel(II) ion.

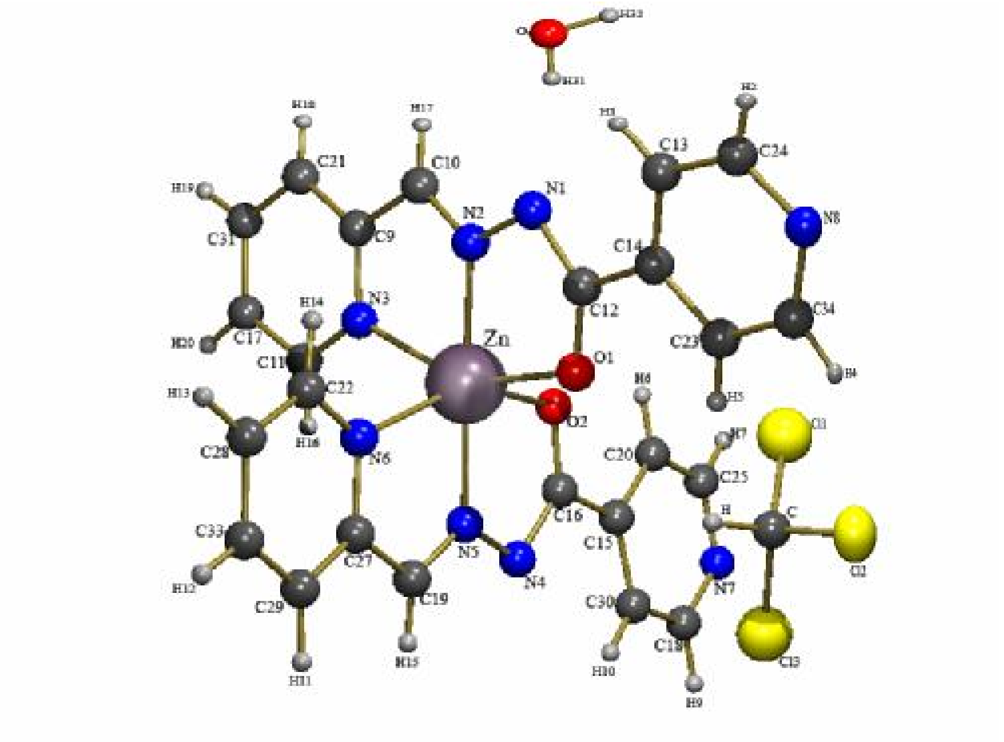


Figure 1. The molecular unit of **6b***1H_2O*1$CHCl_3$ in the crystal, ORTEP representation, 50% probability plot.

The plane of the distorted octahedron around the metal is defined by the two oxygen and two nitrogen atoms, while the two apical positions are occupied by the nitrogen atoms. The distortion of the coordination sphere around the metal is due to the ligand rigidity, this kind of distortion was observed in other similar reported complexes [11, 18].

The angles at Ni center show deviations from the ideal octahedron, for example, N5-Ni-O1 angle: 76.42(8)° and N2-Ni-N3: 78.27(9)° have significant deviation from 90°, while N5-Ni-N2: 174.04(10)° and O1-Ni-N3: 154.70(8)° deviated from ideal 180°.

The two ligands are closely but not fully equivalent in their bond angles and bond distances. Variation of bond lengths are 0.03 Å at most. Intraligand distances are in conformity with the enolate form of both ligands. The distances N1-C12 1.340(4) and N4-C1 1.333(3) are short compared with typical single bond which is 1.52 Å. C12-O1 1.265(3) and C16-O2 1.279(3) are lengthened compared with the normal ketonic bond length which is 1.23 Å.

Small deviation from planarity of the ligand in ***(4a)*** are obvious by looking at the torsion angles:N2-C10-C9-N3 has a dihedral angle of 1.45° and the N1-C12-C14-C13 5.51°.

The structures of ***(4b)*** and ***(6b)*** have the same general description, the same mode of bonding and the same pattern of distortion as ***(4a)***. The angles at the metal center show similar behavior to that of ***(4a)*** except in the N5-Zn-O1 and N5-Ni-O1 which have values 99.97(7) and 100.09(7), respectively. In these complexes also, the two ligands are slightly equivalent in binding to the central metals, details of the values are listed in tables **1** and **2.**

Table 1. Crystal data and Structure Refinement for the complexes **4a**, **4b** and **6b**

Sum formula	**$C_{27}H_{23}Cl_3N_6O_3Ni$ (4a)**	**$C_{25}H_{21}Cl_3N_8O_3Ni$ (4b)**	**$C_{25}H_{21}Cl_3N_8O_3Zn$ (6b)**
Formula weight	644.57	646.56	653.22
Crystal system	triclinic	triclinic	triclinic
a [Å]	11.374	11.188(9)	11.222(9)
b [Å]	11.596	11.445(7)	11.501(7)
c [Å]	11.727	12.004(7)	12.045(7)
α [°]	105.600	107.04(4)	106.63(4)
β [°]	104.304	103.44(5)	102.92(5)
γ [°]	104.985	105.110(6)	106.090(6)
V [Å^3]	1353.2	1337.0(16)	1351.7(16)
T [K]	173	173	173
Z	2	2	2
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
μ [mm^{-1}]	1.056	1.071	1.250
Indep. Reflections (R_{int})	6217 (0.0223)	7834 (0.0225)	7986 (0.0147)
R_1 (obsd. Data)	0.0445	0.0377	0.0315
wR_2	0.1018	0.0907	0.0815
Index ranges	h = -14→15 k = -11→15 l = -15→15	h = -15→14 k = -16→16 l = -17→17	h = -15→15 k = -16→16 l = -16→17
Theta range	1.92-28.01°	1.88-30.50°	1.87-30.52°

Table 2. Principal Bond Distances (Å) and Angles (deg) in **4a**, **4b**, and **6b**

Selected bond lengths [Å]	**$C_{27}H_{23}Cl_3N_6O_3Ni$ (4a)**	**$C_{25}H_{21}Cl_3N_8O_3Ni$ (4b)**	**$C_{25}H_{21}Cl_3N_8O_3Zn$ (6b)**
M-N5	1.976(2)	1.9808(18)	2.0488(16)
M-N2	1.985(2)	1.9876(18)	2.0705(17)
M-O1	2.089(2)	2.109(2)	2.156(2)
M-O2	2.1166(19)	2.1265(17)	2.1315(16)
M-N6	2.119(2)	2.1310(18)	2.2434(17)
M-N3	2.135(2)	2.107(2)	2.188(2)
Selected bond angles [°]	$C_{27}H_{23}Cl_3N_6NiO_3$ (**4a**)	$C_{25}H_{21}Cl_3N_8NiO_3$ (**4b**)	$C_{25}H_{21}Cl_3N_8O_3Zn$ (**6b**)
N5-M-N2	174.04(10)	176.64(6)	172.95(5)
N2-M-O1	76.42(8)	76.59(7)	74.22(6)
N5-M-O2	75.86(8)	76.39(6)	75.12(5)
O1-M-O2	95.03(8)	95.03(8)	98.13(8)
N5-M-N6	78.68(9)	78.29(7)	75.60(6)
N2-M-N3	78.27(9)	78.13(7)	75.95(6)
O2-M-N3	91.32(8)	91.44(8)	92.85(8)
N5-M-O1	97.64(8)	105.19(7)	99.97(7)
N2-M-N6	100.71(9)	102.21(7)	100.19(6)
O1-M-N6	91.39(8)	91.35(8)	90.65(7)
O2-M-N6	154.34(8)	154.59(6)	150.46(5)
N5-M-N3	107.66(9)	105.19(7)	109.69(6)
O1-M-N3	154.70(8)	154.71(6)	150.14(5)
N6-M-N3	93.40(9)	93.21(8)	93.32(7)

Experimental

Melting points (uncorrected) were determined on an electrothermal melting temperature apparatus. ^{1}H- and ^{13}C nmr spectra were recorded on a Brucker 300 MHz instrument for solutions in DMSO-D_6 at 21°C, using TMS as an internal reference. Chemical shifts are expressed in δ(ppm) downfield from TMS. IR spectra were obtained by using Perkin-Elmer 237 infrared specrometer (KBr discs) and mass spectra were measured using electroionization technique.

Ligand synthesis:

The Schiff base ligands (**3a**,**b**) [12] and (**3c**) [13] used in this work were synthesized by condensation of acid hydrazides (**2a-c**) with pyridine-2-carboxaldehyde (**1**) in 1:1 mole ratio in ethanol, some drops of acetic acid were used as a catalyst. The reaction mixture was refluxed for two hours. This gave the corresponding hydrazones in good yields (scheme 1).

2-pyridinecarbaldehyde benzoylhydrazone (HPBH, **3a),** 2-pyridinecarbaldehyde isonicotinoylhydrazone (HPIH, **3b),** 2-pyridinecarbaldehyde thienoylhydrazone (HPTH, **3c)].**

Synthesis of the Complexes

The complexes were prepared by mixing 2.0 mmol of the ligand dissolved in about (30 mL) of methanol, with 1.0 mmol of the metal(II) acetate in (20 mL) hot methanol. The resulting mixture was refluxed for 2-10 hours, the solution was concentrated, then the precipitate was filtered and washed with petroleum ether (40-60 ^{o}C).

The following complexes were prepared using this method:

*Cis-Bis[*2-pyridinecarbaldehyde benzoylhydrazone*]nickel(II)* [$Ni(PBH)_2$] ***(4a)***
From 0.45 g 2-pyridinecarbaldehyde benzoylhydrazone (**3a**), 3 hours reflux: yield 0.41 g (80%) brown, mp. 328 ^{o}C. ESI MS: m/z 507.0 (M+). UV/vis (nm): 371.00, 281.00, 215.00. Significant infrared bands (cm^{-1}): 1602, 1552, 1488, 1463, 1340, 1290, 1141, 1078, 720.

*Cis-Bis[*2-pyridinecarbaldehyde benzoylhydrazone*]copper(II)* [$Cu(PBH)_2$] ***(5a)***
From 0.45 g 2-pyridinecarbaldehyde benzoylhydrazone (**3a**), 10 hours reflux: yield 0.38 g (74%) brown, mp: 222 ^{o}C. ESI MS: m/z 512 (M+). UV/vis (nm): 367.18, 262.39, 213.00. Significant infrared bands (cm^{-1}): 1585, 1552, 1487, 1466, 1333, 1290, 1143, 1068, 719, 521, 416.

*Cis-Bis[*2-pyridinecarbaldehyde benzoylhydrazone*]zinc(II)* [$Zn(PBH)_2$] ***(6a)***
From 0.45 g 2-pyridinecarbaldehyde benzoylhydrazone (**3a**), 5 hours reflux: yield 0.39 g (76%) bright yellow, mp: 320 ^{o}C. ESI MS: m/z 513.0 (M+). UV/vis (nm): 364.18, 286.40, 247.50, 205.13. ^{1}H NMR (D_6-DMSO): δ (ppm) = 7.23-8.74 (Pyr-H, Ph-H), 8.57 (s, CH=N). Significant infrared bands (cm^{-1}): 1585, 1490, 1464, 1340, 1290, 1143, 1068, 721.

*Cis-Bis[*2-pyridinecarbaldehyde isonicotinoylhydrazone*]nickel(II)* [$Ni(PIH)_2$] ***(4b)***
From 0.45 g 2-pyridinecarbaldehyde isonicotinoylhydrazone (**3b**), 4 hours reflux: yield 0.36 g (71%) brown, mp: 331 ^{o}C. ESI MS: m/z 509.0 (M^{+}). UV/vis (nm): 373.87, 276.53, 213.18. Significant infrared bands (cm^{-1}): 1608, 1568, 1487, 1460, 1346, 1304, 1149, 1078, 700, 416.

*Cis-Bis[*2-pyridinecarbaldehyde isonicotinoylhydrazone*]copper(II)* [$Cu(PIH)_2$] ***(5b)***
From 0.45 g 2-pyridinecarbaldehyde isonicotinoylhydrazone (**3b**), 4 hours reflux : yield: 0.43 g (83%) brown, mp: 245 ^{o}C. ESI MS: m/z 514.0 (M+). UV/vis (nm): 369.27, 241.00, 280.00. Significant infrared bands (cm^{-1}): 1600, 1569, 1488, 1458, 1338, 1305, 1151, 1064, 700.

*Cis-Bis[*2-pyridinecarbaldehyde 2'-thienoylhydrazone*]zinc(II)* [$Zn(PIH)_2$] ***(6b)***
From 0.45 g 2-pyridinecarbaldehyde isonicotinoylhydrazone (**3b**), 4 hours reflux: yield 0.41 g (79%) yellow, mp: 326 ^{o}C. ESI MS: m/z 515.0 (M+). UV/vis (nm): 363.52, 281.11, 233.95, 204.05. ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.22-8.86 (Pyr-H, Ph-H), 8.59 (s, CH=N). ^{13}C NMR ($CDCl_3$): δ (ppm) 174.49, 149.29, 148.50, 147.32, 143.50, 14013, 138.92, 125.19, 124.14 and 122.7. Significant infrared bands (cm^{-1}): 1593, 1568, 1487, 1464, 1344, 1310, 1149, 1074, 700.

*Cis-Bis[*2-pyridinecarbaldehyde 2'-thienoylhydrazone*] nickel(II)* [$Ni(PTH)_2$] ***(4c)***
From 0.46 g 2-pyridinecarbaldehyde 2'-thienoylhydrazone (**3c**) , 2 hours reflux: yield: 0.49 g (94%) brown, mp: > 300 ^{o}C. ESI MS: m/z 521.0 (M^{+}). UV/vis (nm): 378.20, 270.00, 233.50, 203.00. Significant infrared bands (cm^{-1}): 1603, 1527, 1494, 1460, 1419, 1358, 1306, 1123, 1072, 852, 710, 411.

*Cis-Bis[*2-pyridinecarbaldehyde 2'-thienoylhydrazone*]copper(II)* [Cu(PTH)$_2$] ***(5c)***
From 0.46 g 2-pyridinecarbaldehyde 2'-thienoylhydrazone (**3c**), 2 hours reflux: yield 0.51 g (97%) brown, mp: 274 ^{o}C. ESI MS: 524.0 (M^+). UV/vis (nm): 376.00, 296.98, 265.24, 236.17, 206.20. Significant infrared bands (cm^{-1}): 1601, 1526, 1489, 1466, 1418, 1356, 1306, 1124, 1070, 847, 710.

*Cis-Bis[*thiophene-2-carboxylic acid pyridine-2-ylmethylene-hydrazid*]zinc(II)* [Zn(PTH)$_2$] ***(6c)***
From 0.46 g 2-pyridinecarbaldehyde 2'-thienoylhydrazone (**3c**), 2 hours reflux: yield: 0.51 g (97%) yellow, mp:350 ^{o}C. ESI MS: m/z 525.0 (M^+). UV/vis (nm): 274.09, 266.00, 231.74. Significant infrared bands (cm^{-1}): 1600, 1550, 1495, 1420, 1367, 1306, 1123, 1080, 1029.

Experimental (of the crystal structures of 4a, 4b and 6b)

Suitable crystals were mounted on Bruker Smart CCD-1000 TM diffractometer and measured at -100 °C, with MoKα radiation source (λ = 0.71073 Å) and graphite monochromator: scan width of 0.3° in ω, measuring 20 sec/frame, and 1800 frames for a full shell up to $\theta = 28°$, no absorption correction. The structures were solved by SHELEXS-93 [16] and refined with SHELXL-97 [16] by full matrix least square parameters on F^2. Graphics were drawn with Mercury program (version 1.4.2) and Platon [17] for windows, the final look performed with the assistance of POV-Ray program (version 3.6). Further details of the crystal structure determination can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, Tel. (+44)1223-336-408, FAX (+44)1223-336-033, E-Mail: deposit@ccde.com.ac.uk by quoting the depository numbers CCDC 650359, CCDC 650360 and CCDC 650361.

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