Synthesis and characterization of three new asymmetric Schiff bases and X-ray crystal structure of [H_2cd3-OMesalen] ligand

S.Menati[a,*], Reza Azadbakht[b], A. Kakanejadi[c], A. Taeb[d] Giuseppe Bruno[e] and Hadi Amiri Rudbari[e]

[a]*Department of Chemistry, Islamic Azad University, Khorramabad, Iran.*

[b]*Department of chemistry, Payame Noor University, Hamedan, Iran*

[c]*Department of Chemistry, University of Lorestan, Lorestan, Iran*

[d]*Department of Chemistry,Science and Research Branch, Islamic Azad University, Tehran, Iran*

[e]*Dipartimento di Chimica Inorganica, Vill. S. Agata, Salita Sperone 31, Universita di Messina 98166 Messina, Italy*

abstract

Three new asymmetric Schiff base compounds, (E)-methyl 2-(2-(2-hydroxy-3-methoxybenzylideneamino)ethylamino)cyclopent-1-enecarbodithioate[H_2cd3-OMesalen] (1), (E)-methyl 2-(2-(3,5-di-*tert*-butyl-2-hydroxybenzylideneamino)ethylamino)cyclopent-1-enecarbodithioate[H_2cd^{di}*tert*butsalen] (2) and (E)-methyl2-(2-(3-hydroxy-4-methoxybenzylideneamino)ethylamino)cyclopent-1-enecarbodithioate[H_2cd4-OMesalen] (3) have been prepared. The compounds have been studied with IR, ^{1}H NMR, ^{13}C NMR and microanalysis. The crystal structure of (1) has been also determined.

Keywords: Schiff base, asymmetric compounds, crystal structure

Introduction

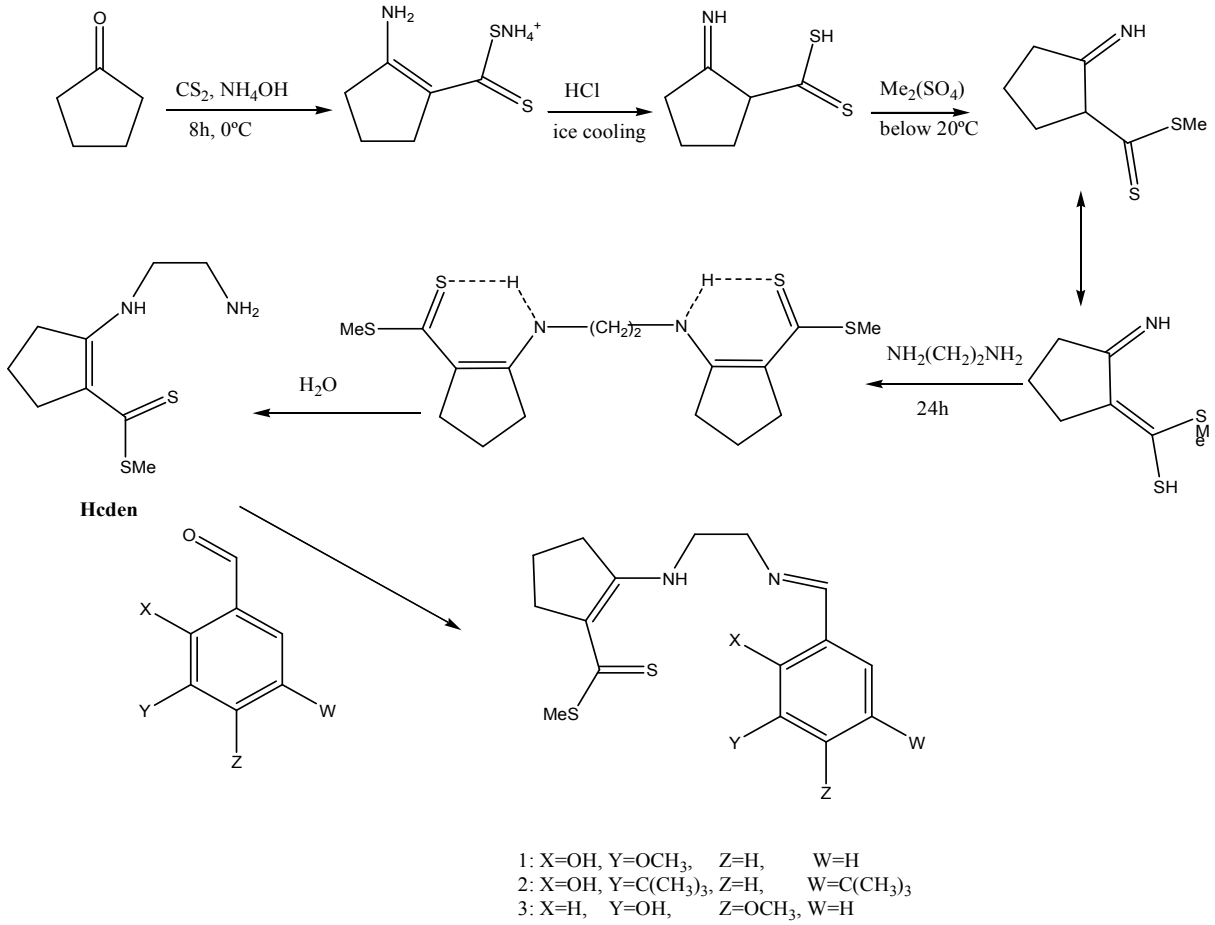
Reflecting their usual relative ease of synthesis and excellent imine bonding properties, Schiff base compounds have been extensively investigated for more than a century and have been

employed in areas that include analytical and bioinorganic chemistry, non-linear optics, fluorescence studies, catalysis and materials chemistry. [1–12] Asymmetric Schiff base compounds have been widely studied in connection with catalysis, due to versatility of their steric and electronic properties.[13-17] The development of simple methods to produce asymmetric products remains an area of considerable research activity.[18] In the other hand, it is well known that, N and S atoms play a key role in the coordination of metals at the active sites of numerous metallobiomolecules. We are particularly interested in synthesis and characterization of the asymmetric Schiff base compounds. In this work, synthesis and characterization of three new asymmetric mono imine Schiff base (1, 2 and 3) is reported. The crystal structure of the compound 1 was determined.

Results and discussion

Synthesis

Methyl-2-{N-(2-aminoethane)}-amino-1-cyclopentenedithiocarboxylate (Hcden) was prepared by literature methods.[19–22] The compounds 1, 2 and 3 were prepared by the addition of an equimolar amount of methanolic solution of the appropriate 2-hydroxy-3-methoxybenzaldehyde, 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde and 3-hydroxy-4-methoxybenzaldehyde to a methanolic solution of Hcden. The products were recrystallized from methanol/chloroform 1:1 (V:V). (see Scheme 1).



1: X=OH, Y=OCH_3, Z=H, W=H
2: X=OH, Y=$C(CH_3)_3$, Z=H, W=$C(CH_3)_3$
3: X=H, Y=OH, Z=OCH_3, W=H

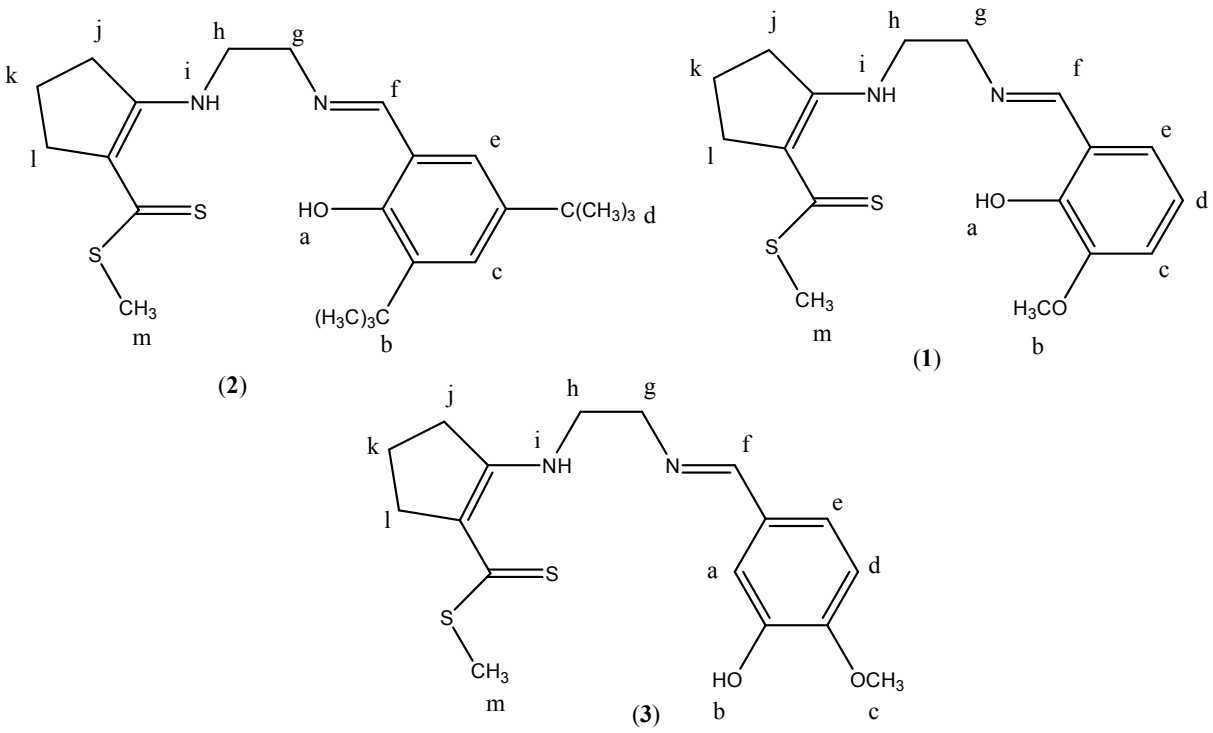
Scheme 1.

All the compounds are yellow, air-stable solids, moderately soluble in organic solvents. The infrared spectra of the compounds confirm the formation of the Schiff bas compounds by the absence of bands characteristic of carbonyl and primary amine groups of the starting materials. The compounds exhibit a Schiff-base ν(C=N) vibration in the range 1652–1654 cm^{-1} and also bands at approximately 3300 cm^{-1} associated with secondary amine groups. The NMR study of the compounds also provides strong evidence for the formation of the Schiff bases. The ^1H NMR spectrum of the compound (1) shows a triplet due to the H_k resonance at ca. 1.81 ppm, a singlet due to the H_m resonance at ca. 2.58 ppm, a multiplet due to the $H_{j,l}$ resonance at ca. 2.77 ppm, a triplet due to the H_h resonance at ca. 3.74 ppm and a triplet due to the H_g resonances at ca. 3.38 ppm, a singlet due to the H_b at ca.3.94 ppm, In the region characteristic of aromatic protons

(6.68–7.46 ppm) four signals were found, The signals of imine proton was appeared at 8.200 ppm and absorption signal of hydroxy proton appears in the region of 12.33. Seventeen, twenty and seventeen resonance are expected in the ^{13}CNMR spectrum of 1, 2 and 3, respectively, but only fifteen, sixteen, and fifteen main signals appeared because of overlap of carbon resonances. The ^{1}H NMR data for compounds of 2 and 3dissolved in $CDCl_3$ are shown in Table1, which uses the lettering scheme shown in Scheme 2.

Table1. ^{1}H NMR spectral assignments for (1) and (2) recorded in $CDCl_3$

Hydrogen atom	δ_H (ppm)	Hydrogen atom	δ_H (ppm)
compound (2)		compound (3)	
Hb(s)	1.45	Ha,d,e	6.84-7.28
Hc,e(s)	7.23, 7.47	Hb(b)	12.37
Hd(d)	1.32	Hc(s)	3.94
Hf(s)	8.44	Hf(s)	8.4
Hg(t)	3.87	Hg(t)	3.89
Hi	3.2	Hh(t)	3.76
Hj,l(m)	2.73	Hj,l(m)	2.75
Hk(qu)	1.8	Hk(qu)	1.81
Hm(s)	2.59	Hm(s)	2.57
Hh(s)	3.84	Hi	3.21



Scheme 2

2.5. Crystal structure determination

Vapour diffusion of ether into a solution of (1) in methanol afforded yellow crystalline needles. Single crystal diffraction data for compound (1) was collected on a Bruker Smart Apex II CCD diffractometer with graphite monochromatic Mo-Ka radiation (k = 0.71073 Å) at room temperature. Data collection, cell refinement, data reduction and absorption correction were performed by multi-scan methods by means of the Bruker software.[1] The structures were solved by direct methods using SIR2004.[2] The non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method on F^2 using SHELXL.[3] All the H atoms were introduced in calculated positions and constrained to ride on their parent atoms. The crystal data and refinement results are given in Table 2. Selected bond distances and angles are given in Table 3, while the molecular structure is shown in Fig. 1.

Table 2
Crystal data and structure refinement for compound 1

Empirical formula	$C_{16}\,H_{17}\,N_2\,O_2\,S_2$
Formula weight	333.44
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	triclinic, P-1
Unit cell dimensions	a = 7.7933(2) A alpha = 108.0380(10) deg.
	b = 10.3486(2) A beta = 93.3490(10) deg.
	c = 11.9532(3) A gamma = 100.2960(10) deg.
Volume	895.19(4) A^3
Z, Calculated density	2, 1.237 Mg/m^3
Absorption coefficient	0.304 mm^-1
F(000)	350
Crystal size	0.25 x 0.30 x 0.40 mm
Theta range for data collection	2.68 to 29.07 deg.
Limiting indices	-10<=h<=10, -14<=k<=14, -16<=l<=16
Reflections collected / unique	34526 / 4762 [R(int) = 0.0189]
Completeness to theta = 29.07	99.50%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4762 / 0 / 212
Goodness-of-fit on F^2	1.366
Final R indices [I>2sigma(I)]	R1 = 0.0391, wR2 = 0.1481
R indices (all data)	R1 = 0.0435, wR2 = 0.1578
Extinction coefficient	0.000(8)
Largest diff. peak and hole	0.361 and -0.203 e.A^-3

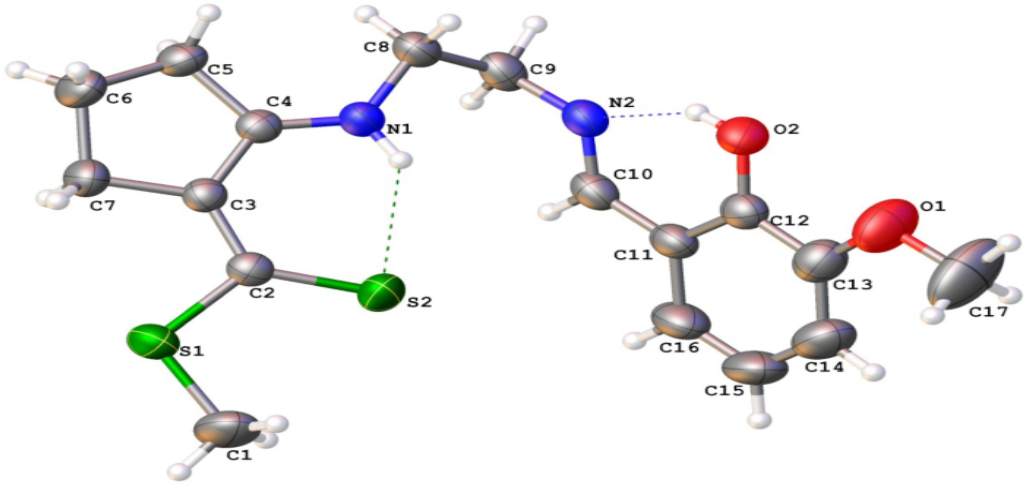


Fig. 1. Crystal structure of (E)-methyl 2-(2-(2-hydroxy-3-methoxybenzylideneamino)ethylamino)cyclopent-1-enecarbodithioate (1)

The compound shows intermolecular O(2)–H……N(2) and N(1)-H……S(2) hydrogen bonding in the range of 1.85 and 2.32 Å, respectively (Table 3).

Table 3. Important bond lengths (Å) and bond angles (˚) for compound 1

Bond	Bond length(Å)	Bond	Bond angle(˚)
C3-C4	1.4059(15)	N(2)-C(10)-C(11)	121.81(11)
N(2)-C(10)	1.2852(14)	C(10)-N(2)-C(9)	119.16(10)
N(2)-C(9)	1.4501(15)	N(2)-C(9)-C(8)	110.34(9)
C(8)-C(9)	1.5153(17)	N(1)-C(8)-C(9)	110.00(9)
N(1)-C(8)	1.4524(14)	C(4)-N(1)-C(8)	126.57(10)
C(2)-C(3)	1.3940(14)	C(2)-S(1)-C(1)	104.68(7)
C(2)-S(2)	1.6916(11)	C(12)-O(2)-H(O2)	109.47
C(2)-S(1)	1.7681(11)		
C(10)-C(11)	1.4519(19)		
N(2)-H(O2)	1.8551(12)		
H(N1)-S(2)	2.3202(14)		

General experimental procedure

All syntheses of the Schiff base compounds were performed under similar conditions. A solution of 2-hydroxy-3-methoxybenzaldehyde, 3,5-di-tert-butyl-2-hydroxybenzaldehyde or 3-hydroxy-4-methoxybenzaldehyde (2 mmol) in absolute MeOH (25 mL) was added dropwise to a hot solution of the appropriate Hcden (2 mmol) in absolute methanol (50 mL). The solution was gently refluxed for 6 h. The color of the solution changed to yellow. The solution was then concentrated in a rotary evaporator to a volume of ca. 15 mL. A precipitate was obtained by standing overnight at 0 ºC.

(E)-methyl2-(2-(2-hydroxy-3-methoxybenzylideneamino)ethylamino)cyclopent-1-enecarbodithioate (1), Yield: 31.3 g (89%). Anal. Calcd for $C_{17}H_{22}N_2O_2S_2$: C, 58.25; H, 6.33;

N, 7.99. Found: C, 58.30; H, 6.29; N, 7.97 %. M.p. 133°C. ^{1}H NMR δ_H (500 MHz, $CDCl_3$): 1.81 (p, -CH_2-, 2H), 2.54(s, 2H), 2.79(m, 4H), 3.74(t, 2H), 3.83(t, 2H), 3.94(s, 3H), 6.86–7.46 (Ar, 3H), 8.20(s,C=N, 1H), 12.33(s, OH, 1H). ^{13}C NMR δ_C (500 MHz, $CDCl_3$): 17.33, 25.01, 30.11, 38.54, 48.99, 54.88, 100.09, 118.32, 122.12, 123,22, 125.50, 150.46, 151.65, 160.42, 161.24, 220.01. IR: 3333 (NH), 1651 (C=N). UV–Vis [λ (nm), ε (M^{-1} cm^{-1}), (acetonitrile)]: 395(15440), 314(8725), 261(8097).

(E)-methyl 2-(2-(3,5-di-tert-butyl-2-hydroxybenzylideneamino) ethylamino)cyclopent-1-enecarbodithioate (2), Yield: 31.3 g (89%). Anal. Calcd for $C_{24}H_{36}N_2OS_2$: C, 66.62; H, 8.39; N, 6.47. Found: C, 66.59; H, 8.42; N, 6.45%. M.p. 168°C. ^{1}H NMR δ_H (500 MHz, $CDCl_3$): 1.33 (s, -tert-Butyl, 9H), 1.43 (s, -tert-Butyl, 9H), 1.81 (p, -CH_2-,2 H),), 2.73(m, 4H), 3.74(t, 2H), 3.78(t, 2H), 3.85(t, 3H), 7.28(s, Ar, 1H),7.44 (s, Ar, 1H), 8.44(s, C=N, 1H), 12.38(s, OH, 1H). ^{13}C NMR δ_C (500 MHz, $CDCl_3$): 17.45, 24.85, 30.08, 31.40, 37.74, 41.29, 48.45, 55.18, 101.12, 125.62, 126.32, 138,02, 141.69, 160.44, 161.29, 220.14. IR: 3332 (NH), 1653 (C=N). UV–Vis [λ (nm), ε (M^{-1} cm^{-1}), (acetonitrile)]: 395(31317), 313(16721), 261(17735).

(E)-methyl 2-(2-(3-hydroxy-4-methoxybenzylideneamino)ethylamino)cyclopent-1-enecarbodithioate (3), Yield: 31.3 g (89%). Anal. Calcd for $C_{17}H_{22}N_2O_2S_2$: C, 58.25; H, 6.33; N, 7.99. Found: C, 58.32; H, 6.26; N, 8.01 %. M.p. 142°C. ^{1}H NMR δ_H (500 MHz, $CDCl_3$): 1.81 (p, -CH_2-, H), 2.54(s, 2H), 2.75(m, 4H), 3.76(t, 2H), 3.89(t, 2H), 3.94(s, 3H), 6.84–6.97 (Ar, 3H), 8.40(s, C=N, 1H), 12.37(s, OH, 1H). ^{13}C NMR δ_C (500 MHz, $CDCl_3$): 17.86, 25.34, 31.31, 38.55, 49.52, 56.64, 100.23, 115.35, 116.52, 123.56, 133.45, 145.34, 153.35, 161.21, 161.36,

220.32. IR: 3330 (NH), 1652 (C=N). UV–Vis [λ (nm), ε (M^{-1} cm^{-1}), (acetonitrile)]: 395(11779), 305(8447), 264(8053).

We are grateful to the Dpartment of chemistry of Azad Islamic Universities, Payame Noor University, Universita di Messina for support of this work.

References:

1. Sabater, M.J.; Alvaro, M.; Garcia, H.; Palomares E.; Sherrington, J.C. ; Chem. Soc. Rev., **1999**, 28, 85.
2. Korupoju, S.R.; Mangayarkarasi, N.; Ameerunisha, S.; Valente E.J.; Zacharias, P.S.; J. Chem. Soc., Dalton Trans., **2000**, 2845.
3. Di Bella, S.; Chem. Soc. Rev., **2001**, 30, 355.
4. Lacroix, P.G.; Eur. J. Inorg. Chem., **2001**, 339.
5. Di Bella, S.; Fragala, I.; Ledoux, I.; Zyss, J.; Chem. Eur. J., **2001**, 7**,** 3738.
6. Di Bella, S.; Fragala, I.; New J. Chem., **2002**, 26**,** 285.
7. Splan, K.E.; Massari, A.M. ; Morris, G.A.; Sun, S.-S.; Eina, E.R.; Nguyen, S.T.; Hupp, J.T.; Eur. J. Inorg. Chem., **2003**, 2348.
8. Hupp, J.T.; Eur. J. Inorg. Chem., **2003**, 2348
9. Evans, C.; Luneau, D.; J. Chem. Soc., Dalton Trans., **2002**, 83.
10. Cozzi, P.G.; Dolci, L.S.; Garelli, A.; Montalti, M.; Prodi,L.; Zaccheroni, N.; New J. Chem., **2003**, 27, 692.
11. Dey, S.K.; Mondal, N.; El Fallah, M.S.; Vicente, R.; Escuer, A.; Solans, X.; Font-Bardia, M.; Matsushita, T.; Gramlich, V.; Mitra, S.; Inorg. Chem., **2004**, 43, 2427.
12. Lecren, L.; Wernsdorfer, W.; Li, Y.-T.; Vindigni, A.; Miyasaka, H.; Cle´rac, R.; J. Amer. Chem. Soc., **2007**, 129**,** 5045.
13. Wang, Y.; Wang, M.; Wang, Y.; Wanga, X.; Wanga, L.; Sun, L.; J. of Catalysis, **2010**, 273**,** 177–181
14. Martinez, A.; Hemmert, C.; Gornitzka, H.; Meunier, B.; J. Organ. Chem., **2005**, 690, 2163–2171.
15. Li, Z.; Liu, G.; Zheng, Z.; Chen, H.; Tetrahedron, **2000**, 56, 7187–7191.
16. Gama, A.; Flores-Lo´ pez, L. Z.; Aguirre, G.; Parra-Hake, M.; Somanathan, R.; Walsh, P. J..; Tetrahedron: Asymmetry, **2002**, 13, 149–154.
17. Baleizão, C.; Gigante, B.; Garcia, H.; Corma, A.; Journal of Catalysis, **2003**, 215, 199–207.
18. GÜngör, Ö.; Gürkan. P.; Spectrochimica Acta Part A, **2010**, 77, 304-311.
19. Bordas, B.; Sohar, P.; Matolcsy, G.; Berencsi, P.; J. Org. Chem., **1972**, 37, 1727.
20. Nag, K.; Joardar, D.S.; Inorg. Chim. Acta, **1975**, 14, 133.
21. Castro, B.; Pereira, E.; Gomes, L.; Inorg. Chim. Acta, **1998**, 271, 83.
22. Nag, K.; Mondal, S.K.; Paul, P.; Roy, R.; Transition Met. Chem., **1984**, 9, 247.