

Synthesis and characterization of copper(II), nickel(II) and cobalt(II) complexes with novel thiourea derivatives

Hakan Arslan* and Nevzat Külçü

Department of Chemistry, Faculty of Arts and Sciences, Mersin University, Mersin, Turkey

Ulrich Flörke

Department of Inorganic and Analytical Chemistry, University of Paderborn, Paderborn, Germany

Received 03 January 2003; accepted 11 March 2003

Abstract

A novel series of thiourea derivatives, namely, *N,N*-diphenyl-*N'*-(4-phenyl-benzoyl)thiourea (HL¹), *N,N*-diphenyl-*N'*-(4-chloro-benzoyl)thiourea (HL²) and *N,N*-di-*n*-propyl-*N'*-(4-chloro-benzoyl)thiourea (HL³), and its metal complexes has been prepared and characterised by elemental analysis, i.r. spectroscopy, ¹H-n.m.r. spectroscopy, mass spectrometry and single crystal X-ray diffraction. The ligand coordinates to Ni^{II}, Cu^{II} and Co^{II} in a bidentate manner yielding essentially neutral complexes of the type *cis*-[ML₂]. N.m.r. spectra and single crystal X-ray diffraction analysis revealed the presence of a distorted tetrahedral coordination ML₂ complex.

Introduction

Cobalt, nickel and copper are essential elements for biological systems and are present in trace quantities. In each case, trace analysis of these elements require pre-concentration prior to their analysis. Thiourea derivatives are selective analytical reagents, especially for the determination of transition metals in complex interfering matrices [1, 2]. The complexing capacity of thiourea derivatives has been reported in several papers [3, 4]. It has been shown that the redox properties of these derivatives are markedly influenced by electronic factors [5–8]. Attachment of transition-metal complexes to electrodes has been investigated intensively in recent years [9]. The biological activity of complexes with thiourea derivatives has been successfully screened for various biological actions. On the other hand some thiourea derivatives have been used in commercial fungicides [10–13].

In previous studies *N,N*-dialkyl-*N'*-benzoylthioureas derivatives having such properties, and their metal complexes, were synthesised and their thermal behaviour examined [14–16]. Based upon the literature search, we could find no synthesis or characterization of these thiourea derivatives (HL¹, HL², and HL³) and their metal complexes. In this paper, we report the preparation and chemical structure properties of HL¹, HL² and HL³ and some of its metal complexes.

Experimental

Instrumentation

I.r. spectra were recorded in the 4000–400 cm⁻¹ range on a Shimadzu 435 spectrophotometer, using KBr pellets. ¹H-n.m.r. spectra were recorded on a Bruker DPX 300 spectrometer, using CDCl₃ as solvent and TMS as internal standard. ¹H-n.m.r. signals were recorded with the aid of 2D COSY spectra where necessary. Mass spectra were recorded on a VG Autospec, using the FAB technique. Elemental analyses were carried out on a Carlo Erba MOD 1106 instrument. Melting points were determined on a digital melting point instrument (Electrothermal model 9200).

Single crystal X-ray data were collected on a Bruker AXS P4 diffractometer using monochromated MoK_α radiation. Standard reflections, monitored after every 300 reflections, showed only random deviations. LP corrections and empirical absorption corrections *via* psi-scans were applied. The structure was solved by direct and conventional Fourier methods. Full-matrix least-squares refinement were based on *F*². Anisotropic atomic displacement parameters were refined for all non-hydrogen atoms; geometrically placed hydrogen atoms were refined using a 'riding model' with *U*(H) = 1.2 *U*(C_{iso}) for most H atoms, but *U*(H) = 1.5 *U*(C_{iso}) for methyl groups. SHELXTL [17] was used for all the calculations. Further details concerning data collection and refinement are given in Table 1.

* Author for correspondence

Table 1. Summary of crystallographic data and parameters of the Ni^{II} complex

Formula	C ₂₈ H ₃₆ Cl ₂ N ₄ NiO ₂ S ₂
Formula weight	654.34
Temperature (K)	203(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
<i>a</i> (Å)	9.438(3)
<i>b</i> (Å)	12.982(2)
<i>c</i> (Å)	13.905(1)
α (°)	65.35(1)
β (°)	87.17(2)
γ (°)	84.10(2)
<i>V</i> (Å ³)	1540.2(6)
<i>Z</i>	2
<i>D_c</i> (mg m ⁻³)	1.411
Absorption coefficient (mm ⁻¹)	0.971
<i>F</i> (0 0 0)	684
Crystal size (mm ³)	0.44 × 0.26 × 0.21
θ range for data collection (°)	2.96–27.50
Index ranges	−1 ≤ <i>h</i> ≤ 12, −15 ≤ <i>k</i> ≤ 15, −18 ≤ <i>l</i> ≤ 18
Reflections collected	8074
Independent reflections (<i>R</i> _{int})	6830 (0.0223)
Absorption correction	Psi-scan
Maximum and minimum transmission	0.750 and 0.582
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	6830/0/348
Goodness-of-fit on <i>F</i> ²	1.049
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0465, <i>wR</i> ₂ = 0.0986
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0841, <i>wR</i> ₂ = 0.1233
Largest diff. peak and hole (e Å ⁻³)	0.718 and −0.560

Synthesis of the ligands

All chemicals used for the preparation of the ligands were of reagent grade quality. A solution of an appropriately substituted benzoyl chloride (0.01 mol) in Me₂CO (50 cm³) was added dropwise to a suspension of KSCN (0.01 mol) in Me₂CO (30 cm³). The reaction mixture was heated under reflux for 30 min, then cooled to room temperature. A solution of secondary amine (0.01 mol) in Me₂CO (10 cm³) was added and the resulting mixture was stirred for 2 h. HCl (0.1 N, 300 cm³) was added and the solution filtered. The solid product was washed with H₂O and purified by recrystallization from EtOH/CH₂Cl₂.

N,N-diphenyl-*N'*-(4-phenyl-benzoyl)thiourea, (*HL*¹): Yellow. Yield: 89%, m.p. 152–154 °C. (Found: C, 76.4; H, 5.0; N, 6.7; C₂₆H₂₀N₂OS calcd.: C, 76.4; H, 4.9; N, 6.9%). I.r. (KBr pellet, cm⁻¹): ν(N—H) 3289 (w, br), ν(C=O) 1690 (s). ¹H-n.m.r. (CDCl₃): 8.83 (s, 1H, NH), 7.70–7.22 (m, 19H, aromatic ring). MS(FAB), *m/z*(%) = 409 (M⁺, 100), 286 (8), 212 (10) and 181 (85).

N,N-diphenyl-*N'*-(4-chloro-benzoyl)thiourea, (*HL*²): Yellow. Yield: 91%, m.p. 159–161 °C. (Found: C, 65.3; H, 4.2; N, 7.7; C₂₀H₁₅N₂OSCl calcd.: C, 65.5; H, 4.1; N, 7.6%). I.r. (KBr pellet, cm⁻¹): ν(N—H) 3206 (w, br), ν(C=O) 1693 (s), ν(C—Cl) 750 (s). ¹H-n.m.r. (CDCl₃): 8.83 (s, 1H, NH), 7.79 (d, 2H, C₆H₄Cl), 7.56–6.89 (m, 12H, aromatic ring). MS(FAB), *m/z*(%) = 367 (M⁺, 100), 287 (43), 244 (77) and 169 (49).

N,N-dipropyl-*N'*-(4-chloro-benzoyl)thiourea, (*HL*³): White. Yield: 87%, m.p. 96–98 °C. (Found: C, 56.4; H, 6.5; N, 9.6; C₁₄H₁₉N₂OSCl calcd.: C, 56.3; H, 6.4; N, 9.4%). I.r. (KBr pellet, cm⁻¹): ν(N—H) 3211 (s, br), ν(C=O) 1686 (s), ν(C—Cl) 750 (w). ¹H-n.m.r. (CDCl₃): 9.16 (s, 1H, NH), 7.81–7.76 (m, 2H, C₆H₄Cl), 7.43–7.32 (m, 2H, C₆H₄Cl), 3.90 (t, 2H, CH₂), 3.46 (t, 2H, CH₂), 1.80 (m, 2H, CH₂), 1.67 (m, 2H, CH₂), 1.00 (t, 3H, CH₃), 0.87 (t, 3H, CH₃). MS(FAB), *m/z*(%) = 299 (M⁺, 100), 267 (8), 255(14) and 139 (74).

Synthesis of the complexes

All chemicals used for the preparation of the complexes were of reagent grade quality. A solution of the metal acetate (0.01 mol) in EtOH (30 cm³) was added dropwise to a solution of the ligand (0.02 mol) in DCM (50 cm³) at room temperature and the resulting mixture was stirred for 30 min. The precipitated complexes were filtered and recrystallized from ethanol/dichloromethane [18, 19].

Bis(*N,N*-diphenyl-*N'*-(4-phenyl-benzoyl)thioureato) nickel(II) [*Ni*(*L*¹)₂]: Red. Yield: 84%, m.p. 294–296 °C. (Found: C, 70.8; H, 4.5; N, 6.2; C₅₂H₃₈N₄O₂S₂Ni calcd.: C, 71.5; H, 4.4; N, 6.4%). I.r. (KBr pellet, cm⁻¹): ν(C=O) 1505 (s). ¹H-n.m.r. (CDCl₃): 8.04 (d, 4H, C₆H₄), 7.69–7.20 (m, 34H, aromatic ring).

Bis(*N,N*-diphenyl-*N'*-(4-phenyl-benzoyl)thioureato)-copper(II) [*Cu*(*L*¹)₂]: Green. Yield: 87%, m.p.

225–227 °C. (Found: C, 71.0; H, 4.5; N, 6.3; $C_{52}H_{38}N_4O_2S_2Cu$ calcd.: 71.1; H, 4.4; N, 6.4%.) I.r. (KBr pellet, cm^{-1}): $\nu(C=O)$ 1503 (s).

Bis(N,N-diphenyl-N'-(4-phenyl-benzoyl)thioureato)cobalt(II) [$Co(L^1)_2$]: Green. Yield: 92%, m.p. 215–216 °C. (Found: C, 72.5; H, 4.6; N, 6.5; $C_{52}H_{38}N_4O_2S_2Co$ calcd.: 71.5; H, 4.4; N, 6.4%.) I.r. (KBr pellet, cm^{-1}): $\nu(C=O)$ 1505 (s). 1H -n.m.r. ($CDCl_3$): 8.01 (d, 4H, C_6H_4), 7.68–7.19 (m, 34H, aromatic ring).

Bis(N,N-diphenyl-N'-(4-chloro-benzoyl)thioureato)nickel(II) [$(Ni(L^2)_2)$]: Red. Yield: 86%, m.p. 297–298 °C. (Found: C, 59.6; H, 3.7; N, 7.0; $C_{40}H_{28}N_4O_2S_2Cl_2Ni$ calcd.: C, 60.8; H, 3.6; N, 7.1%.) I.r. (KBr pellet, cm^{-1}): $\nu(C=O)$ 1504 (s), $\nu(C-Cl)$ 756 (w). 1H -n.m.r. ($CDCl_3$): 7.67 (d, 4H, C_6H_4Cl), 7.39–7.20 (m, 24H, aromatic ring).

Bis(N,N-diphenyl-N'-(4-chloro-benzoyl)thioureato)copper(II) [$Cu(L^2)_2$]: Green. Yield: 85%, m.p. 225–227 °C. (Found: C, 60.1; H, 3.5; N, 6.9; $C_{40}H_{28}N_4O_2S_2Cl_2Cu$ calcd.: C, 60.4; H, 3.5; N, 7.0%.) I.r. (KBr pellet, cm^{-1}): $\nu(C=O)$ 1508 (s), $\nu(C-Cl)$ 755 (w).

Bis(N,N-diphenyl-N'-(4-chloro-benzoyl)thioureato)cobalt(II) [$Co(L^2)_2$]: Green. Yield: 88%, m.p. 227–228 °C. (Found: C, 59.9; H, 3.8; N, 6.9; $C_{40}H_{28}N_4O_2S_2Cl_2Co$ calcd.: C, 60.8; H, 3.6; N, 7.1%.) I.r. (KBr pellet, cm^{-1}): $\nu(C=O)$ 1506 (s), $\nu(C-Cl)$ 755 (w). 1H -n.m.r. ($CDCl_3$): 7.76 (d, 4H, C_6H_4Cl), 7.34–7.13 (m, 24H, aromatic ring).

Bis(N,N-dipropyl-N'-(4-chloro-benzoyl)thioureato)nickel(II) [$Ni(L^3)_2$]: Pink. Yield: 87%, m.p. 188–189 °C. (Found: C, 51.7; H, 5.7; N, 8.5; $C_{28}H_{36}N_4O_2S_2Cl_2Ni$ calcd.: C, 51.4; H, 5.5; N, 8.6%.) I.r. (KBr pellet, cm^{-1}): $\nu(C=O)$ 1508 (s), $\nu(C-Cl)$ 756 (w). 1H -n.m.r. ($CDCl_3$): 8.05–7.99 (m, 4H, C_6H_4Cl), 7.38–7.27 (m, 4H, C_6H_4Cl), 3.72–3.61 (m, 8H, CH_2), 1.82–1.65 (m, 8H, CH_2), 0.98–0.91 (m, 12H, CH_3).

Bis(N,N-dipropyl-N'-(4-chloro-benzoyl)thioureato)copper(II) [$Cu(L^3)_2$]: Green. Yield: 91%, m.p. 145–147 °C. (Found: C, 50.8; H, 5.6; N, 8.4; $C_{28}H_{36}N_4O_2S_2Cl_2Cu$ calcd.: C, 51.0; H, 5.5; N, 8.5%.) I.r. (KBr pellet, cm^{-1}): $\nu(C=O)$ 1514 (s), $\nu(C-Cl)$ 757 (w).

Bis(N,N-dipropyl-N'-(4-chloro-benzoyl)thioureato)cobalt(II) [$Co(L^3)_2$]: Green. Yield: 89%, m.p. 132–134 °C. (Found: C, 51.6; H, 5.6; N, 8.6; $C_{28}H_{36}N_4O_2S_2Cl_2Co$ calcd.: C, 51.4; H, 5.5; N, 8.6%.) I.r. (KBr pellet, cm^{-1}): $\nu(C=O)$ 1508 (s), $\nu(C-Cl)$ 757 (w). 1H -n.m.r. ($CDCl_3$): 8.12–8.07 (m, 4H, C_6H_4Cl), 7.32–7.20 (m, 4H, C_6H_4Cl), 3.76–3.65 (m, 8H, CH_2), 1.83–1.68 (m, 8H, CH_2), 0.99–0.90 (m, 12H, CH_3).

Results and discussion

We report the synthesis and characterization (by elemental analysis, i.r. spectroscopy, 1H -n.m.r. spectroscopy, mass spectrometry and single crystal X-ray diffraction methods) of a novel series of substituted

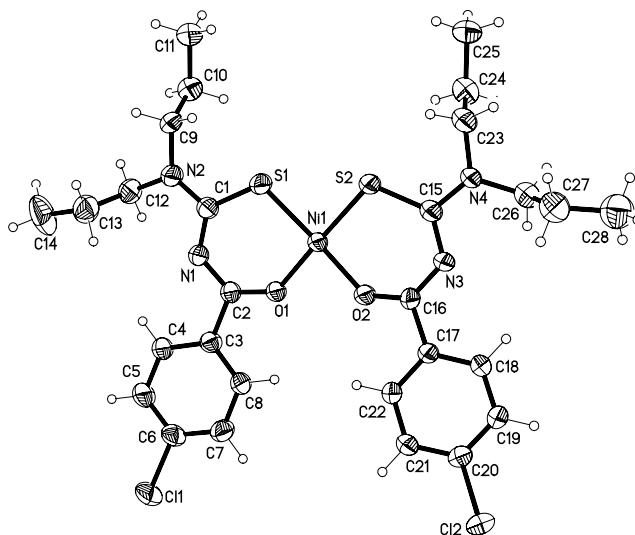


Fig. 1. ORTEP drawing of *cis*-bis(*N,N*-dipropyl-*N'*-(4-chloro-benzoyl)thioureato)nickel(II).

thiourea derivatives and its nickel(II), copper(II) and cobalt(II) complexes.

In the i.r. spectra of the ligands the N—H stretching vibration is observed in the 3200 cm^{-1} region as a broad band. This band disappears upon metal complex formation. Deprotonation induces delocalization and the C=O stretching vibration frequency decreases by *ca.* 180 cm^{-1} in agreement with the literature [20]. This band shift confirms coordination through the oxygen atom. A shift to a higher frequency would also be expected for the C=S stretching vibration, but this vibration could not be assigned unambiguously because of overlap with other bands in the region.

The 1H -n.m.r. spectra of the compounds are consistent with the structural results. The protons were assigned by 1H -n.m.r. and 2D COSY studies. The N—H signal for the ligands in the 8–9 p.p.m. region, disappears upon complexation. This data is in agreement with the i.r. spectra. The 1H -n.m.r. spectra show multiplets at 8.12–6.9 p.p.m. for phenyl protons in the ligand and its metal complexes. The aryl proton signals are shifted to upper field (0.1–0.2 p.p.m.) relatively to those in the free ligand. The methylene protons of the propyl group show two signals at *ca.* 3.9 and 3.5 p.p.m., which represent the rotomer of thiocarbonyl group.

The molecular structure of bis(*N,N*-dipropyl-*N'*-(4-chlorobenzoyl)thioureato)nickel(II) complex showing the atom numbering scheme is given in Figure 1. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2 and selected bond lengths and angles are given in Table 3. The nickel atom is in a four-coordination geometry contributed by two O and two S atoms (S(1)—Ni—O(2) 175.73(9)°, O(1)—Ni—S(2) 177.35(9)°). The dihedral angle between S(1)NiO(1) plane and S(2)NiO(2) plane is 4.5(2)°. The bond lengths of the thiocarbonyl C(1)—S(1) 1.732(4); C(15)—S(2) 1.727(4) Å and carbonyl C(2)—O(1) 1.265(4); C(16)—O(2) 1.268(4) Å bonds are longer than

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for *cis*-bis(*N,N*-dipropyl-*N'*-(4-chlorobenzoyl)thioureato)nickel(II)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Ni(1)	2438(1)	4125(1)	2934(1)	35(1)
S(1)	3500(1)	2945(1)	4348(1)	48(1)
S(2)	854(1)	2940(1)	3322(1)	52(1)
Cl(1)	7114(1)	9809(1)	1231(1)	58(1)
Cl(2)	−1845(1)	10098(1)	−1477(1)	54(1)
O(1)	3824(2)	5155(2)	2534(2)	39(1)
O(2)	1475(2)	5220(2)	1757(2)	44(1)
N(1)	5638(3)	4406(2)	3798(2)	39(1)
N(2)	6012(3)	2692(2)	5185(2)	44(1)
N(3)	−651(3)	4524(2)	1587(2)	41(1)
N(4)	−1375(3)	2754(2)	2388(3)	53(1)
C(1)	5133(4)	3405(3)	4422(3)	38(1)
C(2)	4950(3)	5196(3)	2968(3)	35(1)
C(3)	5588(4)	6310(3)	2474(3)	37(1)
C(4)	6800(4)	6494(3)	2882(3)	45(1)
C(5)	7295(4)	7564(3)	2481(3)	50(1)
C(6)	6557(4)	8444(3)	1678(3)	43(1)
C(7)	5376(4)	8283(3)	1232(3)	46(1)
C(8)	4891(4)	7204(3)	1646(3)	43(1)
C(9)	5592(4)	1630(3)	6031(3)	43(1)
C(10)	6080(4)	587(3)	5842(3)	51(1)
C(11)	5584(5)	−477(3)	6731(3)	62(1)
C(12)	7511(4)	2948(3)	5233(3)	47(1)
C(13)	7631(5)	3598(4)	5886(4)	58(1)
C(14)	9219(5)	3643(5)	6067(5)	94(2)
C(15)	−438(4)	3464(3)	2356(3)	43(1)
C(16)	234(4)	5312(3)	1402(3)	35(1)
C(17)	−284(3)	6490(3)	666(3)	34(1)
C(18)	−1443(4)	6711(3)	15(3)	48(1)
C(19)	−1918(4)	7805(3)	−652(3)	53(1)
C(20)	−1237(4)	8693(3)	−653(3)	41(1)
C(21)	−79(4)	8505(3)	−17(3)	38(1)
C(22)	393(4)	7401(3)	641(3)	36(1)
C(23)	−1508(4)	1631(3)	3292(3)	51(1)
C(24)	−697(5)	692(3)	3106(3)	59(1)
C(25)	−1047(5)	−461(3)	3976(4)	67(1)
C(26)	−2368(4)	3023(3)	1480(3)	53(1)
C(27)	−3762(5)	3522(4)	1668(4)	64(1)
C(28)	−4847(5)	3507(4)	867(4)	75(1)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

Table 3. Selected bond lengths (\AA) and angles ($^\circ$) of the Ni^{II} complex

Bond lengths			
Ni—O(1)	1.864(2)	O(1)—C(2)	1.265(4)
Ni—O(2)	1.862(2)	O(2)—C(16)	1.268(4)
Ni—S(1)	2.1415(11)	N(1)—C(1)	1.347(4)
Ni—S(2)	2.1421(11)	N(1)—C(2)	1.325(4)
S(1)—C(1)	1.732(4)	N(3)—C(15)	1.347(4)
S(2)—C(15)	1.727(4)	N(3)—C(16)	1.321(4)
Bond angles			
O(1)—Ni—O(2)	83.99(10)	O(2)—Ni—S(1)	175.73(9)
O(1)—Ni—S(1)	94.97(8)	O(2)—Ni—S(2)	94.59(8)
O(1)—Ni—S(2)	177.35(9)	S(1)—Ni—S(2)	86.60(4)

the average for C=S and C=O, while the C—N bonds in the complex ring are all shorter than the average for C—N single bonds. These results indicate extensive delocalization of electrons within the complex ring of

the compounds, which is supported by the i.r. data. All the other bond lengths fall within the expected range. According to all of the results, our studies have shown that bis(*N,N*-dipropyl-*N'*-(4-chlorobenzoyl)thioureato)-nickel(II) complex preferentially form neutral *cis*-[NiL₂] type complex as presented in Figure 1.

Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data [CCDC-185157] can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

This work was supported by Mersin University Research Fund (project no: FEF.K.HA.99.1). We thank Dr H.A. Dondas for the interpretation of ¹H-n.m.r. spectra.

References

1. M. Schuster, *Fresen. J. Anal. Chem.*, **342**, 791 (1992).
2. M. Merdivan, *The Analysis of Platinum Metals in Platinum Catalysts by Thin Layer Chromatography*, Ph.D thesis, Middle East Technical University, Ankara, Turkey, 1994.
3. M. Schuster, B. Kugler and K.H. König, *Fresen. J. Anal. Chem.*, **338**, 717 (1990).
4. K.H. König, M. Schuster, G. Schneeweis and B. Steinbrech, *Zeit. Anal. Chem.*, **319**, 66 (1984).
5. M. Guttman, K.H. Lubert and L. Beyer, *Fresen. J. Anal. Chem.*, **356**, 263 (1996).
6. E. Guillon, G. Mohamadou, I. Déchamps-Olivier and J.P. Barbier, *Polyhedron*, **15**, 947 (1996).
7. A. Mohamadou, I. Dechamps-Olivier and J.P. Barbier, *Polyhedron*, **13**, 3277 (1994).
8. I. Dechamps-Olivier, E. Guillon, A. Mohamadou and J.P. Barbier, *Polyhedron*, **15**, 3617 (1996).
9. J. Losada, D.I. Peso and L. Beyer, *Transition Metal Chem.*, **25**, 112 (2000).
10. F.A. Frech and E.J. Blanz, *Cancer Res.*, **25**, 1454 (1965).
11. E.J. Blanz and F.A. Frech, *Cancer Res.*, **28**, 2419 (1968).
12. F.A. Frech and E.J. Blanz, *J. Med. Chem.*, **9**, 585 (1966).
13. F.A. Frech, E.J. Blanz, J.R.D. Amaral and D.A. French, *J. Med. Chem.*, **13**, 1117 (1970).
14. N. Ozpozan, T. Ozpozan, H. Arslan, F. Karipcin and N. Külcü, *Thermochim. Acta*, **336**, 97 (1999).
15. N. Ozpozan, H. Arslan, T. Ozpozan, N. Ozdes and N. Külcü, *Thermochim. Acta*, **343**, 127 (2000).
16. N. Ozpozan, H. Arslan, T. Ozpozan, M. Merdivan and N. Külcü, *J. Ther. Anal.*, **61**, 955 (2000).
17. G.M. Sheldrick, SHELXTL v. 5.1, *Structure Determination Software Suite*, Bruker AXS, Madison, Wisconsin, USA, 1998.
18. I.B. Douglass and F.B. Dains, *J. Am. Chem. Soc.*, **56**, 719 (1934).
19. L. Beyer, E. Hoyer, H. Henning, R. Kirmse, H. Hartman and J. Liebscher, *J. Prakt. Chem.*, **317**, 265 (1975).
20. M. Mikami, I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **23A**, 1037 (1967).