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Mono- and Binuclear Complexes of Iron(III) with 1,2-*Bis*(2-hydroxybenzamido)ethane

Zdeněk Smékal*, **Zdeněk Šindelář**, and **Roman Klička**

Department of Inorganic and Physical Chemistry, Palacký University, CZ-77147 Olomouc, Czech Republic

Summary. Complexes of the type $[(Fe(L))_2O]\cdot H_2O$ (H_2L = 1,2-*bis*(2-hydroxybenzamido)ethane), $[(Fe(L))_2ter]\cdot 5H_2O$ H_2ter = terephthalic acid), $[Fe(L)bpy]BPh_4$ (*bpy* = 2,2′-bipyridyl), and $[Fe(L)phen]ClO_4\cdot H_2O$ (*phen* = *o*-phenanthroline) were prepared and studied by elemental analysis, magnetochemical measurements, and spectroscopic methods. $[(Fe(L))_2O]\cdot H_2O$ and $[(Fe(L))_2ter]\cdot 5H_2O$ are probably binuclear, and the weak antiferromagnetic exchange interaction, (μ_{eff} per one atom of iron(III) was found to be 3.59 BM/77 K–4.91 BM/290 K ($J = -7\,cm^{-1}$, $H = -2JS_1S_2$, $S_1 = S_2 = 5/2$) for the μ-oxo complex and 4.21 BM/82 K–5.35 BM/297 K ($J = -5\,cm^{-1}$) for the μ-terephthalato complex. The iron(III) complexes with *bpy* or *phen* are probably mononuclear; their anomalous μ_{eff} values (3.51 BM/80 K–3.68 BM/297 K for $(Fe(L)bpy]BPh_4$ and 4.93 BM/259 K for $[Fe(L)phen]ClO_4\cdot H_2O$, respectively) agree neither with high spin (5.7–6.1 BM) nor with low spin (2.1–2.5 BM) configurations.

Keywords. Iron(III) complexes; Magnetic properties, Antiferromagnetism; 1,2-*Bis*(2-hydroxybenzamido)ethane.

Mono- und binukleare Eisen(II)-Komplexe mit 1,2-*Bis*(2-hydroxybenzamido)ethan

Zusammenfassung. Komplexe des Typs $[(Fe(L))_2O]\cdot H_2O$ (H_2L = 1,2-*Bis*(2-hydroxybenzamido)-ethan), $[(Fe(L))_2ter]\cdot 5H_2O$ (H_2ter = Terephthalsäure), $[Fe(L)bpy]BPh_4$ (*bpy* = 2,2′-Bipyridyl) und $[Fe(L)phen]ClO_4\cdot H_2O$ (*phen* = *o*-Phenanthrolin) wurden hergestellt und mittels Elementaranalyse, magnetochemischer Messungen und spektroskopischer Methoden untersucht. $[(Fe(L))_2O]\cdot H_2O$ und $[(Fe(L))_2ter]\cdot 5H_2O$ sind wahrscheinlich binuklear, und die schwache antiferromagnetische Austauschwechselwirkung (μ_{eff} pro Eisen(III)-Atom) wurde für den μ-oxo-Komplex zu 3.59 BM/77 K–4.91 BM/290 K ($J = -7\,cm^{-1}$, $H = -2JS_1S_2$, $S_1 = S_2 = 5/2$) und für den μ-terephthalato-Komplex zu 4.21 BM/82 K–5.35 BM/297 K ($J = -5\,cm^{-1}$) ermittelt. Die Eisen(III)-Komplexe mit *bpy* bzw. *phen* sind wahrscheinlich mononuklear; ihre anomalen μ_{eff}-Werte (3.41 BM/80 K–3.68 BM/297 K für $[Fe(L)bpy]BPh_4$ und 4.93 BM/259 K für $[Fe(L)phen]ClO_4\cdot H_2O$ sind weder mit *high-spin*- (5.7–6.1 BM) noch mit *low-spin*-Zuständen (2.1–2.5 BM) in Einklang zu bringen.

Introduction

The aim of this work was the preparation and physicochemical investigation of new complexes of iron(III) with tetradentate amides derived from salicylic acid and

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* Corresponding author

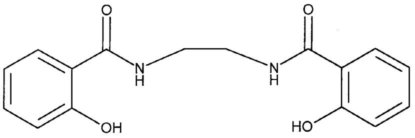

Fig. 1. 1,2-*Bis*(2-hydroxybenzamido)ethane (H_2L)

ethylenediamine in a molar ratio of 2:1 ($H_2L = $ 1,2-*bis*(2-hydroxybenzamido)-ethane) (Fig. 1) and their comparison with complexes of iron(III) with analogous *Schiff* bases (H_2*salen* (N,N′-*bis*(salicylidene)ethylenediamine), H_2*salpn* (N,N′-*bis*(salicylidene)propylenediamine), and H_2*saloph* (N,N′-*bis*(salicylidene)-*o*-phenylenediamine)). We found only few articles in the literature about complexes with 1,2-*bis*(2-hydroxybenzamido)ethane (H_4L). *Liao et al.* [1–5] have synthesized the copper(II) complex $Na_2[Cu(L)] \cdot 5H_2O$ and binuclear complexes with exchange interaction between the central atoms of the compositions $[Cu(L)Mn(L')_2]$, $[Cu(L)Fe(L')Cl]$, $[Cu(L)Cu(L')]$, and $[Cu(L)Ni(L')_2]$ ($L' = $ 2,2′-bipyridine (*bpy*) or *o*-phenanthroline (*phen*)). The copper(II) atom is four-coordinated (by two deprotonated phenolic oxygens and two deprotonated nitrogens from amide groups) in the square-planar arrangement. The oxygen atoms from the phenolic groups form bridges in the above mentioned binuclear compounds, and the ligand 1,2-*bis*(2-hydroxybenzamido)ethane appears as dianion (L^{2-}) against tetraanion (L^{4-}) in *Liao*'s complexes. The mononuclear complexes [Fe(L)*bpy*]BPh_4 (**1**) and [Fe(L)*phen*]$ClO_4 \cdot H_2O$ (**2**) were prepared by reaction of H_2L, $FeCl_3 \cdot 6H_2O$, Et_3N, MeONa, and *bpy* with $NaBPh_4$ or *phen* $\cdot H_2O$ with $LiClO_4 \cdot 3H_2O$. The μ-oxo complex $[(Fe(L))_2O] \cdot H_2O$ (**3**) was obtained by reaction of H_2L, $FeCl_3 \cdot 6H_2O$, and aqueous NH_3 in methanol, and the μ-terephthalato complex $[(Fe(L))_2$*ter*$] \cdot 5H_2O$ (**4**) from the μ-oxo complex and terephthalic acid (H_2*ter*). The compounds were characterized by elemental analysis, IR and UV/Vis spectroscopy and variable temperature magnetic susceptibility measurements (77–297 K).

Results and Discussion

The chemical compositions of the substances prepared are given in Table 1, the data from physico-chemical studies in Tables 2–6 and Figs. 2–4.

The IR spectra were not studied in detail; only the characteristic vibration ν(C=O) was interpreted [6] (Table 2). It appears at $1640\,cm^{-1}$ in free H_2L; in the

Table 1. Chemical compositions of the complexes

	Found (Calcd.) (%)				
	C	H	N	Cl	Fe
$[(Fe(L))_2O] \cdot H_2O$	51.8 (51.8)	4.4 (4.1)	7.2 (7.6)	–	14.5 (15.1)
$[(Fe(L))_2$*ter*$] \cdot 5H_2O$	49.5 (49.9)	4.7 (4.4)	6.1 (5.8)	–	12.3 (11.6)
[Fe(L)*bpy*)BPh_4	72.2 (72.4)	5.0 (5.1)	7.2 (6.8)	–	–
[Fe(L)*phen*]$ClO_4 \cdot H_2O$	51.8 (51.6)	3.8 (3.7)	8.6 (8.6)	4.9 (5.4)	–

Table 2. Magnetic and IR spectroscopic properties of the complexes

	μ_{eff} (BM)/T (K)[a]	IR (cm^{-1}) ν(C=O)
$[(Fe(L))_2O] \cdot H_2O$	3.59/77–4.91/290	1604 m
$[(Fe(L))_2 ter] \cdot 5H_2O$	4.21/82–5.35/297	1604 m
$[Fe(L)bpy)]BPh_4$	3.51/80–3.68/297	1604 m
$[Fe(L)phen]ClO_4 \cdot H_2O$	4.93/295	1600 m

[a] Per atom of iron(III)

Table 3. UV/Vis spectroscopic properties of the complexes

	Colour	UV/Vis (nm)[a]
$[(Fe(L))_2O] \cdot H_2O$	red	516, 633 sh
$[(Fe(L))_2 ter] \cdot 5H_2O$	red	506, 560 sh
$[Fe(L)bpy)]BPh_4$	red	440, 705 sh, 740
$[Fe(L)phen]ClO_4 \cdot H_2O$	brown	570

[a] Diffuse-reflectance spectra

Table 4. Magnetic properties of $[(Fe(L))_2O] \cdot H_2O$

T (K)	χ_M ($cm^3 \cdot mol^{-1}$)[a]	μ_{eff} (BM)
290.3	0.0207	6.94
261.4	0.0227	6.89
224.6	0.0256	6.78
166.1	0.0317	6.49
123.5	0.0373	6.07
110.6	0.0390	5.87
86.0	0.0411	5.32
76.6	0.0419	5.07

[a] Molar susceptibility per molecule corrected for diamagnetism

complexes, ν(C=O) is shifted to about 1600–1604 cm^{-1}, indicating the coordination of the ligand to the iron(III).

There is no information about the electronic structure of iron(III) from diffuse-reflectance UV/Vis spectra (Table 3). Only charge-transfer bands were observed which are in accordance with data for iron(III) complexes with organic ligands [7]. The electronic spectra of solutions of the compounds in dimethylformamide are dissimilar to the diffuse-reflectance spectra. The complexes are instable in dimethylformamide solutions.

A magnetochemical study of $[(Fe(L))_2O] \cdot H_2O$ (**3**) and $[(Fe(L))_2 ter] \cdot 5H_2O$ (**4**) was performed in the range of 77–297 K (Tables 4 and 5, Figs. 2 and 3). The magnetic moments per atom of iron(III) decrease with decreasing temperature from 4.91 BM at 290 K to 3.59 BM at 77 K for $[(Fe(L))_2O] \cdot H_2O$ and from 5.35 BM at

Table 5. Magnetic properties of $[(Fe(L))_2ter] \cdot 5H_2O$

T (K)	χ_M ($cm^3 \cdot mol^{-1}$)	μ_{eff} (BM)
296.8	0.0241	7.56
270.1	0.0263	7.54
220.3	0.0307	7.35
186.4	0.0350	7.22
158.2	0.0395	7.07
135.1	0.0437	6.87
118.5	0.0471	6.68
106.3	0.0497	6.50
91.1	0.0519	6.15
81.7	0.0541	5.95

[a] Molar susceptibility per molecule corrected for diamagnetism

Table 6. Magnetic properties of $[Fe(L)bpy]BPh_4$

T (K)	χ_M ($cm^3 \cdot mol^{-1}$)	μ_{eff} (BM)
296.8	0.00571	3.68
265.1	0.00654	3.72
235.4	0.00725	3.69
180.6	0.00925	3.66
148.1	0.0112	3.65
125.7	0.0131	3.63
98.3	0.0163	3.58
80.2	0.0192	3.51

[a] Molar susceptibility corrected for diamagnetism

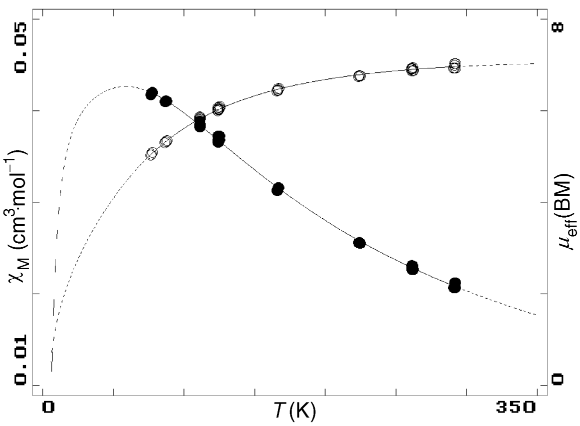

Fig. 2. Paramagnetic susceptibility χ_M (●, $cm^3 \cdot mol^{-1}$) and effective magnetic moment μ_{eff} (○, BM) *vs.* temperature for $[(Fe(L))_2O] \cdot H_2O$ (**3**); circles: experimental, solid lines: calculated according to Eq. (1)

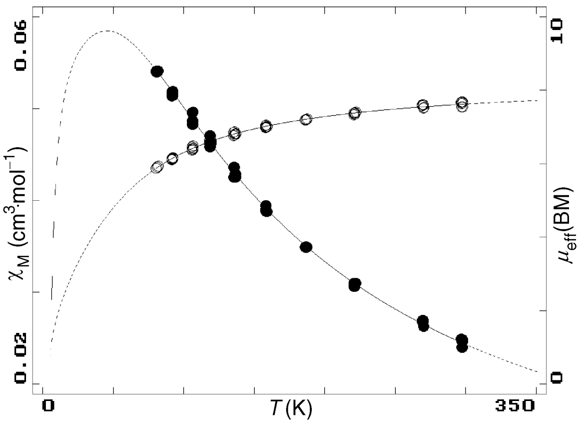

Fig. 3. Paramagnetic susceptibility χ_M (●, $cm^3 \cdot mol^{-1}$) and effective magnetic moment μ_{eff} (○, BM) *vs.* temperature for $[(Fe(L))_2ter] \cdot 5H_2O$ (**4**); circles: experimental, solid lines: calculated according to Eq. (1)

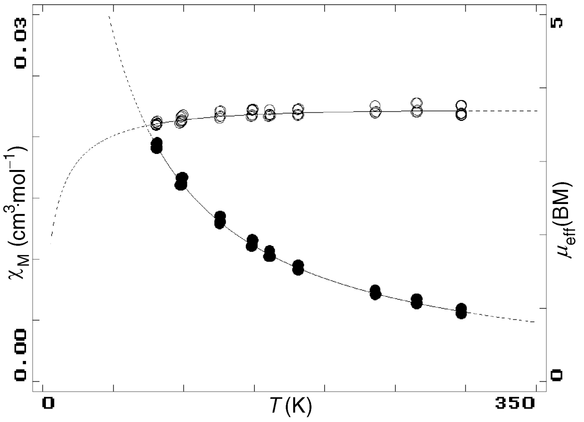

Fig. 4. Paramagnetic susceptibility χ_M (●, $cm^3 \cdot mol^{-1}$) and effective magnetic moment μ_{eff} (○, BM) *vs.* temperature for $[(Fe(L)bpy]BPh_4$ (**1**); circles: experimental, solid lines: calculated according to *Curie-Weiss*' law

297 K to 4.21 BM at 82 K for $[(Fe(L))_2ter] \cdot 5H_2O$. The complexes behaves like iron(III) binuclear compounds ($H = -2JS_1S_2$, $S_1 = S_2 = 5/2$). An expression for the molar paramagnetic susceptibility for an $S_1 = S_2 = 5/2$ exchange-coupled binuclear compound has been presented [8] (Eq. 1):

$$\chi_M = \left(\frac{Ng^2\beta^2}{kT}\right)\frac{2A + 10B + 28C + 60D + 110E}{1 + 3A + 5B + 7C + 9D + 11E} + N_\alpha \qquad (1)$$

The exponentional terms are: $A = \exp(2J/kT)$, $B = \exp(6J/kT)$, $C = \exp(12J/kT)$, $D = \exp(20J/kT)$, and $E = \exp(30J/kT)$; N_α, g, β, k and T have their usual meaning (χ_M is the molar susceptibility per molecule corrected for diamagnetism). A least-square fitting program [9] was used to fit the data for the Fe(III) complexes to the above mentioned equation. The best parameters are $J = -7\,\mathrm{cm}^{-1}$, $g = 2.0$, and $N_\alpha = 0$ for the μ-oxo complex and $J = -5\,\mathrm{cm}^{-1}$, $g = 2.0$ and $N_\alpha = 0$ for the μ-terephthalato complex. A comparison of the values of the exchange integrals J of compounds **3** and **4** with those of compounds with analogous *Schiff* bases (H_2*salen*, H_2*salpn*, and H_2*saloph*) reveal that $[(Fe(L))_2O] \cdot H_2O$ is weakly antiferromagnetic against [(Fe(*salen*))$_2$O] ($J = -95\,\mathrm{cm}^{-1}$), [(Fe(*salpn*))$_2$O] ($J = -90\,\mathrm{cm}^{-1}$) and [(Fe(*saloph*))$_2$O] ($J = -95\,\mathrm{cm}^{-1}$) [10]. [(Fe(*samen*))$_2$*ter*]$\cdot 5H_2O$ as well as [(Fe(*saloph*))$_2$*ter*] show weak antiferromagnetism ($J = ca.\ -5\,\mathrm{cm}^{-1}$); no exchange interaction was found for [(Fe(*salen*))$_2$*ter*] [11].

The compounds [Fe(*L*)*bpy*]BPh$_4$ (**1**) and [Fe(*L*)*phen*]ClO$_4 \cdot H_2O$ (**2**) described in this paper are probably mononuclear octahedral complexes, but their unusual magnetic moments are neither in agreement with high-spin (5.7–6.1 BM) nor low-spin (2.1–2.5 BM) configuration [12]. Regarding their anomalous μ_{eff} values (3.68 BM (**1**) or 4.93 BM (**2**) at room temperature), the temperature dependence of the magnetic susceptibility of [Fe(*L*)*bpy*]BPh$_4$ was measured. It obeyes the *Curie-Weiss* law ($C = 2.0\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1}$, $\theta = -19\,\mathrm{K}$). Upon lowering the temperature, the magnetic moment decreases (3.68 BM/297 K–3.51 BM/80 K) (Table 6, Fig. 4). The magnetic properties of **1** and **2** can be compared with those of complexes with analogous *Schiff* bases (H_2*salen* and H_2*saloph*). Recently [11, 13, 14], octahedral complexes of the types [Fe(*salen*)*L*]BPh$_4$ (*L* = *bpy* or *phen*) and [Fe(*saloph*)*L*]ClO$_4$ (*L* = *bpy* or *phen*) have been characterized. It has been found that the compounds with *salen* have high-spin (S = 5/2) and those with saloph have low-spin (S = 1/2) configuration. *Saloph* has a stronger ligand field than *salen*. The origin of the anomalous magnetic moments of compounds **1** and **2** is unknown.

The newly prepared compounds $[(Fe(L))_2O] \cdot H_2O$ and [(Fe(*L*))$_2$*ter*]$\cdot 5H_2O$ are probably binuclear complexes in which each iron(III) atom is coordinated by the tetradentate amide and by an oxygen bridge (Fig. 5) or by two oxygens from terephthalato bridge. The complexes [Fe(*L*)*bpy*]BPh$_4$ and [Fe(*L*)*phen*]ClO$_4 \cdot H_2O$ are probably mononuclear octahedral complexes (donors atoms are two nitrogens from *bpy* or *phen*, two oxygens from phenolic groups, and two nitrogens from amide groups).

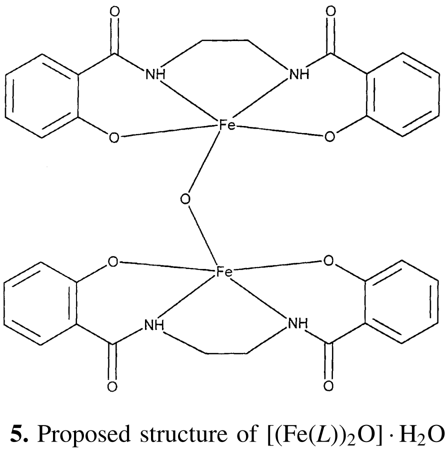

Fig. 5. Proposed structure of $[(Fe(L))_2O] \cdot H_2O$ (**3**)

Experimental

Materials and Methods

Methyl salicylate (p.a.): Riedel-de Haen AG, Seelze-Hannover; ethylenediamine (p.a) and triethylamine (p.): Downs Development Chemicals Limited; $FeCl_3 \cdot 6H_2O$ (p.a.): Winlab Limited, Maindenhead, Berkshire, UK; sodium terephthalate (p.a.): VEB Laborchemie Apolda. All chemicals were used without further purification. $LiClO_4 \cdot 3H_2O$ was prepared by reaction of $HClO_4$ (Carlo Erba) and $LiOH \cdot H_2O$ (Lachema Brno).

Elemental analyses (carbon, hydrogen, and nitrogen) were performed on a Fisons Instruments EA 1108 CHN analyzer. The Fe content was determined thermogravimetrically as Fe_2O_3 after thermal decomposition of the samples. The content of chlorine was estimated by the Schoniger method. Electron diffuse-reflectance or absorption spectra were run on a Specord M40 in Nujol or in dimethylformamide solutions. IR spectra were recorded on a Specord IR 80 instrument in Nujol mulls. The magnetic susceptibility was measured using the *Faraday* method on a magnetic balance constructed in our laboratory. The temperature dependence of magnetic susceptibilities was measured in the range of 77–297 K. $Hg[Co(SCN)_4]$ was used as a calibrant, and diamagnetic corrections were made with *Pascal*'s constants for all constituent atoms.

Syntheses

1,2-Bis(2-hydroxybenzamido)ethane (H_2L)

63.2 ml (0.49 mmol) of methyl salicylate were added to 16.3 ml (0.24 mmol) of ethylenediamine. The reaction mixture was refluxed for 5 hours. After cooling a solid was obtained. The amide was recrystallized three times from hot methanol. The white product was filtered off, washed with a small amount of cold methanol, and dried under an infralamp at 40°C. The yield was 20 g (27%). The substance is well soluble in hot ethanol and hot methanol and insoluble in water; m.p.: 183.5°C.

$[Fe(L)bpy]BPh_4$

A solution of 0.90 g (3.3 mmol) of $FeCl_3 \cdot 6H_2O$ in 10 ml of ethanol was added to a solution of 1.00 g (3.3 mmol) of H_2L in 15 ml of warm ethanol. To the stirred reaction mixture, 0.20 ml (1.4 mmol) of triethylamine were added dropwise. After short reflux (10 min), solutions of MeONa in methanol (10 ml, $c = 0.22\,mol \cdot dm^{-3}$) and of 0.52 g (3.3 mmol) of *bpy* in 5 ml of ethanol were added. After short reflux (15 min), 1.13 g (3.3 mmol) of $NaBPh_4$ in 10 ml of ethanol was added to the well stirred hot reaction mixture. The precipitate was filtered off, washed properly with water, ethanol, and diethyl ether and dried at 40°C. The yield was 0.5 g (20%). The product is insoluble in water, methanol, and ethanol and soluble in dimethylformamide.

$[Fe(L)phen]ClO_4 \cdot H_2O$

This substance was obtained using the same method as described for the preparation of $[Fe(L)bpy]BPh_4$ (starting materials: 0.65 g (3.3 mmol) of $phen \cdot H_2O$ and 0.53 g (3.3 mmol) of $LiClO_4 \cdot 3H_2O$; the product precipitated after concentration to one half of the volume and addition of 15 ml of diethyl ether with some delay). The yield was 0.25 g (10%). The product is insoluble in water, partially soluble in methanol and ethanol, and soluble in dimethylformamide and nitromethane.

$[(Fe(L))_2O] \cdot H_2O$

A solution of 1.80 g (6.6 mmol) of $FeCl_3 \cdot 6H_2O$ in 20 ml of methanol was added to a solution of 2.00 g (6.6 mmol) of H_2L in 20 ml of hot methanol. The colour turned to purple. Then, a solution of NH_3 in methanol (the solution was prepared by mixing of 10 ml of 26% aqueous NH_3 and 50 ml of methanol) was added dropwise to the well-stirred hot reaction mixture until it was alkaline. The precipitate formed was filtered off, washed with ethanol and methanol, and dried at 40°C. The yield was 2.0 g (80%). The product is insoluble in water, methanol, ethanol and nitromethane, and soluble in dimethylformamide and dimethylsulfoxide.

$[Fe(L))_2ter] \cdot 5H_2O$

A solution of 0.08 g (0.49 mmol) of terephthalic acid in 10 ml of nitromethane was added to a suspension of 0.37 g (0.49 mmol) of $[(Fe(L))_2O] \cdot H_2O$ in 15 ml of nitromethane. The well-stirred reaction mixture was refluxed for 3 hours. After cooling the solid was filtered off, washed with methanol and diethyl ether, and dried at 40°C. The yield was 0.4 g (85%). The product is insoluble in water, methanol, ethanol, and nitromethane and soluble in dimethylformamide.

Acknowledgements

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