Available online at www.sciencedirect.com

ScienceDirect

Dyes and Pigments 74 (2007) 636–641

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Synthesis and EPR studies of metallophthalocyanines containing four carbhexyloxybiphenyloxy substituents

Ayfer Kalkan [a], Sadık Güner [b], Zehra Altuntaş Bayır [a,*]

[a] *Department of Chemistry, Technical University of Istanbul, TR34469 Maslak, Istanbul, Turkey*
[b] *Department of Physics, Fatih University, TR34500 Büyükçekmece, Istanbul, Turkey*

Received 21 March 2006; received in revised form 19 April 2006; accepted 20 April 2006
Available online 5 June 2006

Abstract

4-(4′-Carbhexyloxybiphenyloxy)phthalonitrile was synthesized by esterification of 4-(4′-carboxybiphenyloxy)phthalonitrile with hexanol in the presence of dicyclohexylcarbodiimide (DCCI). Zn(II), Co(II) and Cu(II) phthalocyanines with four carbhexyloxybiphenyloxy pendant groups on the periphery were prepared from 4-(4′-carbhexyloxybiphenyloxy)phthalonitrile and the corresponding divalent metal salts ($Zn(CH_3COO)_2$, $CoCl_2$ and $CuCl_2$). These new compounds have been characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, UV–vis and mass spectroscopies. The EPR spectra obtained at room temperature indicate axially symmetric character of ligand field at the site of Co(II) and Cu(II) paramagnetic ions. Especially, the Cu(II) coordinated compounds show stronger covalency effects with neighboring N atoms with respect to Co(II) coordinated compounds. Computer programs have been written to determine Spin–Hamiltonian parameters for solid powder form of ion coordinated complexes. Orbital energy levels for magnetic electrons were determined from Spin–Hamiltonian parameters as well.

Keywords: Phthalocyanine; Zinc; Cobalt; Copper; EPR

1. Introduction

Phthalocyanines, a family of aromatic macrocycles based on an extensive delocalized 18-π electron system, are known not only as classical dyes in practical use but also as modern functional materials in scientific researches [1]. There has been growing interest in the use of phthalocyanines in a variety of new high technology fields including semiconductor devices [2], Langmuir–Blodgett films [3], electrochromic display devices [4], gas sensors [5], liquid crystals [6], nonlinear optics [7], photodynamic cancer therapy [8,9] and various catalytic processes [10]. The attractive and challenging characteristics of phthalocyanines in these applications arise from their great variety, thermal and chemical stability, redox versatility and intense colour.

Phthalocyanines usually constitute a group of crystalline compounds, whose insolubility in organic solvents is a common characteristic. Improving the solubility of phthalocyanines is an important factor for the investigation of their properties in solvents. Phthalocyanine derivatives of increased solubility have been obtained using electron-donating substituents such as alkyl, alkoxy, alkylthio chains, and bulky groups, or electron-withdrawing substituents such as chloro, bromo, and nitro moieties [11–18]. Because of their lower degree of order in the solid state, tetra-substituted phthalocyanines are more soluble than the corresponding octasubstituted ones. The introduction of sulfonyl, carboxyl or amino groups results in water soluble derivatives [19–21]. Quaternized ammonium groups are especially useful in providing solubility within a wide pH range [22].

A remarkable feature of phthalocyanines is their ability to form a wide range of condensed phases with controlled molecular architectures, such as liquid crystals and thin films, which may exhibit responses at a supramolecular level. A large variety of liquid crystalline phthalocyanine derivatives containing

---

* Corresponding author. Tel.: +90 212 285 32 23; fax: +90 212 285 63 86.
E-mail address: bayir@itu.edu.tr (Z.A. Bayır).

0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.04.003

different aliphatic tails, including alkyl, alkylcarbonyloxy, alkoxy chains and crown ethers have been synthesized [23–26].

The transition metal ions coordinated to molecules offer new ways to induce, modify and control molecular properties. Especially paramagnetic properties are well investigated by the Electron Paramagnetic Resonance (EPR) technique, which provides information about the elemental composition, electronic structure of paramagnetic states and nuclearity. The effective and apparent g (Lande splitting factor) values are used to assess the spin state of a molecule [27–31]. The number of hyperfine lines and the magnitude of hyperfine coupling constant can be used to identify the nuclei to which the unpaired electrons are coupled.

Our previous papers have described a series of phthalocyanines substituted with macrocyclic/acyclic groups starting mostly from 4-nitrophthalonitrile or 4,5-dichlorophthalonitrile [32–36]. In this work, we report the synthesis and characterization of novel soluble metallophthalocyanines having carbhexyloxybiphenyloxy groups on the periphery. Also, paramagnetic properties of Cu(II) and Co(II) phthalocyanines have been studied by using EPR technique at room temperature.

2. Experimental

IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer and electronic spectra on a Unicam UV2 spectrophotometer. ^{1}H NMR spectra were recorded on Bruker 250 MHz and Inova 500 spectrometers using TMS as internal reference. Mass spectra were performed on Varian 711 mass spectrometer. All reagents and solvents were of reagent grade quality obtained from commercial suppliers. The homogeneity of the products was tested in each step by TLC. All solvents were dried and purified as described by Perrin and Armarego [37]. The solvents were stored over molecular sieves. 4-Nitrophthalonitrile [38] and 4-(4′-carboxybiphenyloxy)phthalonitrile (**1**) [39] were prepared by reported procedures.

Co^{2+} and Cu^{2+} coordinated metallophthalocyanines have been investigated by using Electron Paramagnetic Resonance (EPR) technique at room temperature. The EPR spectra of Cu^{2+} and Co^{2+} coordinated compounds in powder forms have been recorded by a conventional X-band ($\nu = 9.5–9.85$ GHz) Bruker EMX model spectrometer employing an ac magnetic modulation technique.

2.1. 4-(4′-Carbhexyloxybiphenyloxy)phthalonitrile (2)

A mixture of 4-(4′-carboxybiphenyloxy)phthalonitrile, **1** (0.50 g, 1.47 mmol), dicyclohexylcarbodiimide (DCCI) (0.90 g, 4.41 mmol), p-toluenesulfonic acid (0.28 g, 1.47 mmol) and 1-hexanol (0.53 ml, 4.41 mmol) was stirred in dry pyridine (25 ml) at room temperature under N_2 for 48 h. As the reaction proceeded, dicyclohexylurea precipitate was formed. Dicyclohexylurea by-product was filtered off and the pale beige filtrate was evaporated to dryness in vacuum. The residue was dissolved in chloroform (20 ml) and washed first with aqueous 10% Na_2CO_3 solution (100 ml) and then with water. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated in vacuo. The crude product was treated with 20 ml CH_2Cl_2 for 2 days at 0 °C to remove the remaining dicyclohexylurea. Finally the white product was obtained by column chromatography with silica gel using $CHCl_3$ as eluent. Yield: 0.37 g (61%); m.p. 98 °C. IR ν_{max}/cm^{-1}: 3075 (Ar–H), 2959–2857 (alkyl CH), 2227 (C≡N), 1710 (C=O), 1588, 1523, 1488, 1274, 1250 (C–O–C), 1183, 1099, 1007, 842, 773. ^{1}H NMR ($CDCl_3$): $\delta = 8.14$ (d, 2H, Ar–H), 7.76–7.62 (m, 5H, Ar–H), 7.32 (d, 1H, Ar–H), 7.28 (d, 1H, Ar–H), 7.18 (d, 2H, Ar–H), 4.33 (t, 2H, OCH_2), 1.78 (q, 2H, $OCCH_2$), 1.45–1.24 (m, 6H, CCH_2C), 0.90 (t, 3H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, APT): 166.62 (C=O), 161.79 (aromatic C), 153.93 (biphenyl C), 144.22 (biphenyl C), 138.55 (biphenyl C), 135.71 (aromatic CH), 130.47 (biphenyl CH), 130.03 (biphenyl C), 129.78 (biphenyl CH), 127.19 (biphenyl CH), 121.92 (aromatic CH), 121.86 (aromatic CH), 121.26 (biphenyl CH), 118.04 (aromatic C), 115.52 (C≡N), 115.11 (C≡N), 109.45 (aromatic C), 65.53 (OCH_2), 31.67, 28.96, 25.96, 22.79 (CH_2), 14.24 (CH_3). UV–vis λ_{max} (nm) (log ε) in THF: 270 (4.98).

2.2. 2,9,16,23-Tetrakis (4′-carbhexyloxybiphenyloxy)phthalocyaninatozinc(II) (3)

A mixture of dinitrile **2** (0.35 g, 0.83 mmol), anhydrous $Zn(CH_3COO)_2$ (0.04 g, 0.21 mmol) and 62 µl of DBU in n-hexanol (2.5 ml) was heated at 150 °C with stirring for 24 h under N_2. The reaction mixture was cooled to room temperature and then diluted with methanol until the crude product precipitated. The precipitate was filtered off and washed several times with hot ethanol and methanol to remove unreacted materials. Finally the bluish-green precipitate was chromatographed on silica gel and eluted with $CHCl_3$:CCl_4 (5:1). Yield: 0.19 g (54%); m.p. > 200 °C. IR ν_{max}/cm^{-1}: 3037 (Ar–H), 2926–2856 (alkyl CH), 1713 (C=O), 1599, 1521, 1468, 1268, 1230 (C–O–C), 1181, 1097, 1005, 826, 770. ^{1}H NMR ($CDCl_3$): $\delta = 7.91–7.45$ (m, 44H, Ar–H), 4.21 (t, 8H, OCH_2), 1.71–1.24 (m, 32H, CCH_2C), 0.90 (t, 12H, CH_3). UV–vis λ_{max} (nm) (log ε) in THF: 287 (4.58), 349 (4.48), 609 (4.26), 675 (4.95). MS (FAB): m/z 1764.46 $[M]^+$.

2.3. 2,9,16,23-Tetrakis (4′-carbhexyloxybiphenyloxy)phthalocyaninatocobalt(II) (4)

A mixture of **2** (0.30 g, 0.71 mmol), anhydrous $CoCl_2$ (0.02 g, 0.18 mmol) and 53 µl of DBU was refluxed in n-hexanol (2 ml) with stirring for 24 h under N_2. The resulting suspension was cooled to room temperature and the crude product was precipitated by the addition of methanol. It was centrifuged and washed first with ethanol and then with methanol. The blue product was obtained on silica gel with $CHCl_3$:MeOH (50:5) as eluent. Yield: 0.10 g (33%); m.p. > 200 °C. IR ν_{max}/cm^{-1}: 3037 (Ar–H), 2922–2852 (alkyl CH), 1713 (C=O), 1599, 1521, 1467, 1267, 1232 (C–O–C), 1180, 1094, 1004, 825, 770. UV–vis λ_{max} (nm) (log ε) in THF: 284 (4.93), 325 (4.86), 601 (4.32), 664 (4.98). MS (FAB): *m/z* 1755.06 $[M]^+$.

*2.4. 2,9,16,23-Tetrakis (4′-carbhexyloxybiphenyloxy)phthalocyaninatocopper(II) (**5**)*

Compound **2** (0.20 g, 0.47 mmol) and anhydrous $CuCl_2$ (0.02 g, 0.12 mmol) were refluxed in *n*-hexanol (1.5 ml) in the presence of 35 μl of DBU under N_2 with stirring for 24 h. After cooling to room temperature the blue mixture was treated with MeOH to precipitate the product completely. The precipitate was filtered off and washed with ethanol and acetone. The product was purified by column chromatography with silica gel using $CHCl_3$ as eluent. Yield: 0.06 g (29%); m.p. > 200 °C. IR ν_{max}/cm^{-1}: 3037 (Ar–H), 2927–2856 (alkyl CH), 1712 (C=O), 1599, 1522, 1465, 1267, 1231 (C–O–C), 1180, 1095, 1005, 824, 769. UV–vis λ_{max} (nm) (log ε) in THF: 292 (4.61), 348 (4.39), 608 (4.07), 676 (4.89). MS (FAB): *m/z* 635.23 $[M - 4(C_{19}H_{21}O_2)]^+$.

3. Results and discussion

3.1. Synthesis

Scheme 1 shows the synthetic route of tetra-substituted metallophthalocyanines. Recently, we have reported the synthesis of biphenylcarboxylic acid substituted phthalocyanines. To improve the solubility, hexyl substituents were introduced into the biphenyl units of the metal-free phthalocyanine [39]. Also the same route was applied to prepare metallophthalocyanines, but we could not synthesize metallophthlocyanines with this method because of the difficulties in purification. To overcome this difficulty, firstly 4-(4′-carboxybiphenyloxy)phthalonitrile (**1**) was reacted with hexanol and then converted into metallophthalocyanines. 4-(4′-Carbhexyloxybiphenyloxy) phthalonitrile (**2**) was synthesized by treating **1** with hexanol in pyridine in the presence of dicyclohexylcarbodiimide (DCCI) and *p*-toluenesulfonic acid as catalyst for 48 h at room temperature. The function of DCCI was to facilitate the formation of ester bond by forming an activated ester. Dicyclohexylurea by-product was separated from the crude product by treatment with dichloromethane for 2 days at 0 °C and then filtered off.

The peripherally tetra-substituted metallophthalocyanines (Zn(II), Co(II), and Cu(II)) (**3**–**5**) were prepared from the phthalonitrile derivative **2** and corresponding anhydrous metal chloride (or acetate) catalyzed by DBU in 1-hexanol. The yield of **3**–**5** was much higher than that obtained using other methods mentioned above. Separation of the phthalocyanines from the product mixture was achieved by column chromatography. The blue-green phthalocyanines are soluble in a number of solvents such as THF, CH_2Cl_2, and $CHCl_3$.

All these new compounds were characterized by elemental analysis, ^1H and ^{13}C NMR, UV–vis, IR and mass spectroscopies. Comparison of the IR spectra at each step gave some insights on the nature of the products. In the IR spectrum of dinitrile compound **2**, aliphatic C–H and C≡N stretching vibrations appeared at 2959–2857 and 2227 cm^{-1}, respectively. This sharp C≡N peak disappeared in the IR spectra of the phthalocyanines. In addition, the characteristic vibrations of the C=O and aromatic C–O–C were observed at 1710 and 1250 cm^{-1}, respectively. ^1H NMR spectrum of **2** exhibited the OCH_2, $OCCH_2$ protons at δ 4.33 and 1.78 ppm as a triplet and a quintet, the aliphatic CH_3 protons as a triplet at δ 0.90 ppm and the aromatic protons at around δ 8.14–7.18 ppm. The ^{13}C NMR spectrum of **2** indicated protonated aromatic and unsaturated carbon atoms at δ 161.79–109.45 ppm. Alkyl carbon atoms appeared in the range at δ 31.67–14.24 ppm. Also the nitrile carbons were observed at 115.52 and 115.11 ppm.

The IR spectra of phthalocyanines **3**–**5** are very similar. IR spectra of all **3**–**5** phthalocyanines showed aliphatic C–H, C=O and C–O–C peaks at around 2926–2856, 1713 and 1230 cm^{-1}, respectively. In the ^1H NMR analyses of **3**, the aromatic protons appeared at δ 7.91–7.45 ppm, the OCH_2 protons at δ 4.21 ppm, the aliphatic CH_3 protons at δ 0.90 ppm and the $OCCH_2$ protons at δ 1.71–1.24 ppm, respectively. The ^1H NMR spectra of **3** have the broad absorptions, when compared with that of the dicyano derivative **2**. It is likely that this broadness is due to both chemical exchange caused by aggregation–disaggregation equilibria and the fact that the product obtained in these reactions is a mixture of four positional isomers which are expected to show chemical shifts differing only slightly from each other.

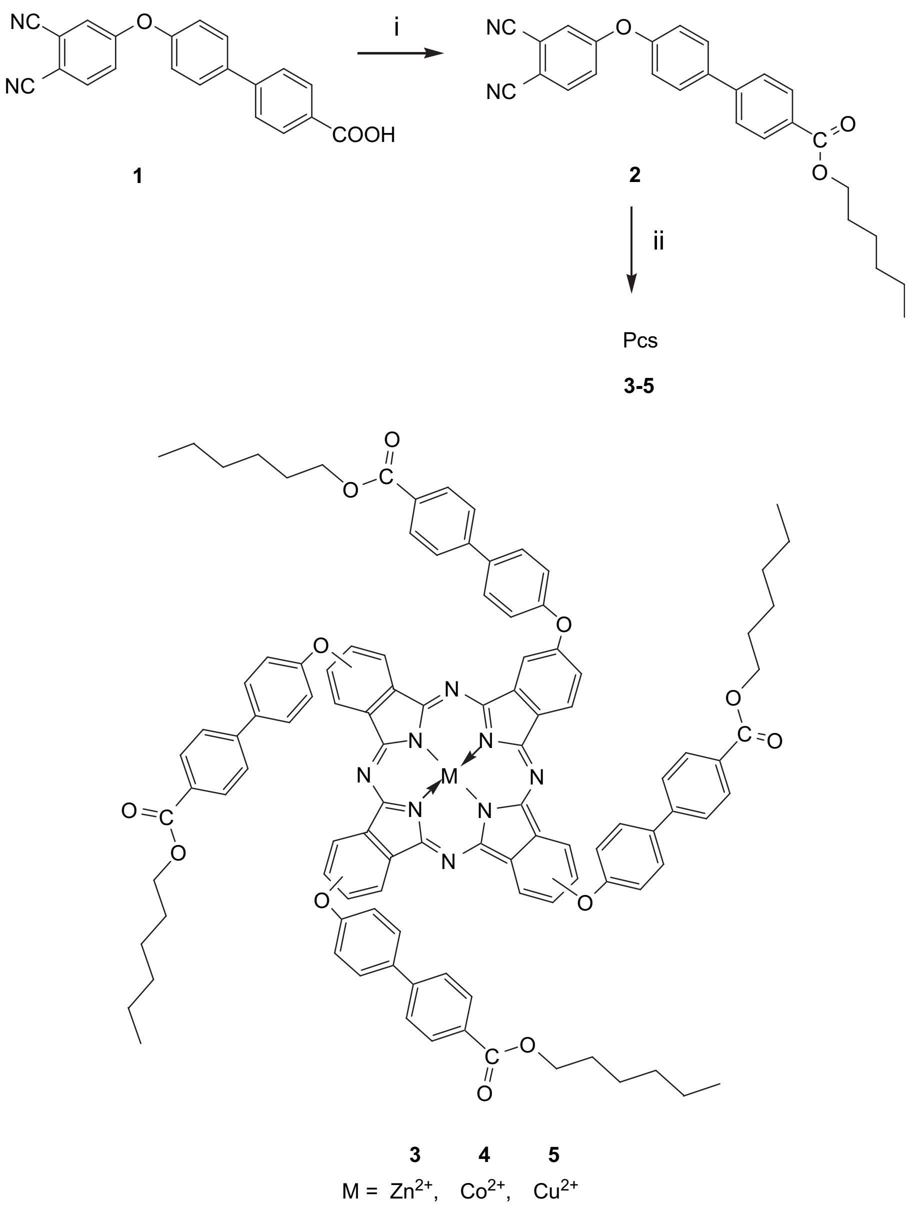
In the FAB mass spectra of the phthalocyanines the presence of the characteristic molecular ion peaks at $m/z = 1764.46$ $[M]^+$ (**3**), 1755.06 $[M]^+$ (**4**) and 635.23 $[M - 4(C_{19}H_{21}O_2)]^+$ (**5**) confirmed the proposed structure.

UV–vis spectra of phthalocyanines are dominated by two intense bands, an ultraviolet Soret (B) band around 300–350 nm and a visible Q band around 600–700 nm [40,41]. UV–vis spectra of **3**–**5** exhibited intense single Q band absorption of the $\pi \rightarrow \pi^*$ transitions at 675, 664 and 676, respectively. B bands of these phthalocyanines appeared in the UV region at around 349–325 nm.

3.2. EPR investigations

3.2.1. Cu^{2+} coordinated complex

The experimental and theoretically fitted EPR signals of Cu^{2+} ion coordinated metallophthalocyanine having four carbhexyloxybiphenyloxy groups in powder form are shown in Fig. 1. The signal has an asymmetric line shape; that is, the positive side of curve is narrower and shorter with respect to the negative side. Furthermore there are no hyperfine lines separated from the main curve. In spite of these observations, the theoretical studies have proved that the magnetic ion has the uniaxial symmetry and theoretical spectrum has exactly fitted with experimental one as can be seen in Fig. 1. The reason for the absence of hyperfine structure could be attributed to the stronger covalency of Cu electrons with neighboring N atoms that causes extra uncertainty of spin energy levels due to interactions with N nuclear spins. Therefore the hyperfine splitting



Scheme 1. Synthetic route of the phthalonitrile derivative (**2**) and the phthalocyanines (**3–5**). (i) *n*-Hexanol, DCCI, *p*-toluenesulfonic acid, and pyridine; (ii) metal salts, DBU, and *n*-hexanol.

becomes weaker and these hyperfine lines completely disappear due to additional broadening of energy levels by superhyperfine interactions of the electronic spins that spent relatively more time around N nuclei [29]. In the literature, there are some given expressions and comparisons that give much information about the magnetic copper ion, such as an expression related with anisotropic $g_\perp = 2.06$ and $g_\parallel = 2.10$ values (these g-values, respectively, denote the effective Lande splitting factors when the external DC field is perpendicular, $B_\perp$ and parallel, $B_\parallel$ to the symmetry axis of the crystalline field around the paramagnetic center), $G = (g_\parallel - 2)/(g_\perp - 2) = 1.67$ and when G is evaluated to be less than 4, supports the exchange interaction among Cu^{2+} ions as well [27]. In addition, there is a general trend about the orbital energy levels for d electrons of copper (Cu^{2+}) ion that if $g_\parallel > g_\perp > 2$ then this means unpaired magnetic electron locates mainly in the $d_{x^2-y^2}$ orbital ($^2B_1$ as ground state) [29].

Hamiltonian equation describing the anisotropic Zeeman interaction includes an additional term of dipolar interaction. The angular dependent dipolar term creates a first-order contribution and can be given as

$$H_{\text{aiso}} = \beta_e\left(g_\perp\left(B_x\cdot J_x + B_y\cdot J_y\right) + g_\parallel(B_z\cdot J_z)\right) + \delta A\left(3\cos^2\theta - 1\right)S_z I_z \qquad (1)$$

where, β_e is the Bohr magneton, S_z and I_z are the electronic and nuclear spins of magnetic electron of Cu^{2+} ion in parallel geometry with respect to the symmetry axis, respectively, J_z is the parallel component of total angular momentum of

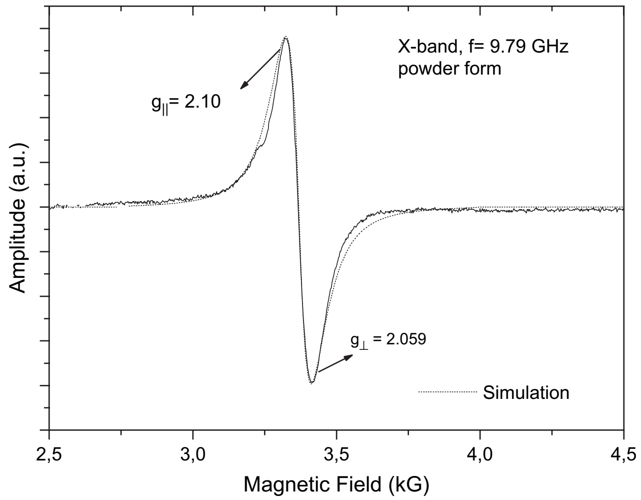


Fig. 1. X-band EPR spectrum of Cu^{2+} coordinated complex compound in powder form at room temperature.

magnetic ion, δA is the dipolar constant and has an expansion given in Ref. [28].

3.2.2. Co^{2+} coordinated complex

The first-derivative EPR signal has been recorded from Co^{2+} ion coordinated metallophthalocyanine in solid powder form with simulated spectra and isshown in Fig. 2. The signal has a characteristic and anisotropic line shape that specifies a uniaxial symmetry for compound with $g_\perp = 2.35 > g_\parallel = 2.05$. In the spectrum, there are well resolved 5 hyperfine peaks at perpendicular part, but it is not possible to determine the number of weak hyperfine peaks at the parallel side. As well known, the 8 hyperfine peaks are expected due to the interaction between the electronic spin of magnetic electron and nuclear spin of $Co^{2+}(I = 7/2)$ ion for both parallel and perpendicular parts of spectrum. However, it can be considered that covalency is decreased as it is compared with the spectrum registered from Cu^{2+} coordinated complex. The decrease in the covalency gives stronger hyperfine interactions with the nucleus of paramagnetic ion and thus the hyperfine components are resolved more clearly. Nevertheless, overlapping and line broadening effects are still observed strongly on splittings, especially in the parallel part.

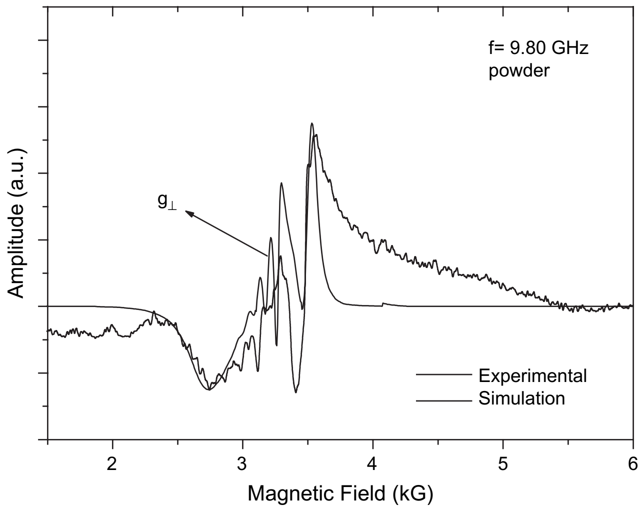


Fig. 2. X-band EPR spectrum of Co^{2+} coordinated complex compound in powder form at room temperature.

In the literature, it is possible to observe $g_\parallel$ values greater than $g_\perp$ registered from some other phthalocyanine compounds in solid powder form [29]. This situation depends on the electronic configuration of metal and symmetry type of powder crystallites. In order to explain the axially symmetric feature of paramagnetic center, we assumed a Hamiltonian containing anisotropic Zeeman and hyperfine interactions as

$$H_{\text{aiso}} = \beta_e \left(g_\perp \left(B_x \cdot J_x + B_y \cdot J_y \right) + g_\parallel (B_z \cdot J_z) \right) + A_\perp \left(I_x \cdot J_x + I_y \cdot J_y \right) + A_\parallel (I_z \cdot J_z) \tag{2}$$

where, $A_\perp$ and $A_\parallel$ are the hyperfine coupling constants for $B_\perp$ and $B_\parallel$, respectively.

The line width characteristic of the hyperfine lines has been fitted according to an equation depending on both M_I (nuclear spin quantum number) and angle [18]. In the literature, it is mentioned for all Co^{2+} coordinated phthalocyanines that they are stable square planar systems with unpaired electron in the d_z^2 orbital perpendicular to the molecular plane, as indicated by $g_\parallel$ being very close to the free electron ($g_e = 2.0023$) splitting value [42]. As seen in Fig. 2, our fit parameters of $g_\parallel$ for both powder forms are also very near to the free electron splitting factor. That is, we can say that magnetic electron is localized in d_z^2 orbital and stable structure of metallophthalocyanine compound is maintained.

The most compatible simulated spectrum with the experimental one has been obtained by using Lorenztian line shape function containing hyperfine parameters, $A_\perp = 140G$ and $A_\parallel = 5G$.

4. Conclusion

In conclusion, we have described the synthesis and spectral characterization of new metallophthalocyanines with carbhexyloxybiphenyloxy groups on the periphery. The distinctive property of these compounds is that they have a good solubility in polar organic solvents.

The EPR spectra indicate axial symmetry around paramagnetic Cu^{2+} and Co^{2+} ions coordinated metallophthalocyanine compounds. Spin–Hamiltonian parameters fitted well. Orbital energy levels for magnetic electrons were obtained from Spin–Hamiltonian parameters as well. Especially Cu^{2+} coordinated compound shows stronger covalency effects with neighboring N atoms.

Acknowledgements

This work was supported by the Research Fund of the Technical University of Istanbul and State Planning Organization (DPT).

References

[1] Leznoff CC, Lever ABP, editors. Phthalocyanines: properties and applications, vols. 1−4. Weinheim: VCH; 1989−1996.

[2] Hanack M, Lang M. Adv Mater 1994;6:819−33.

[3] Cook MJ, McKeown NB, Simmons JM, Thomson AJ, Daniel MF, Harrison KJ, et al. J Mater Chem 1991;1:121−7.

[4] Schlettwein D, Wöhrle D, Jaeger NI. J Electrochem Soc 1989;136:2882−6.

[5] Dogo S, Germain JP, Maleysson C, Pauly A. Thin Solid Films 1992;219:251−6.

[6] Simon J, Sirlin C. Pure Appl Chem 1989;61:1625−9.

[7] Torre de la G, Vazquez P, Agullo-Lopez F, Torres T. J Mater Chem 1998;8:1671−83.

[8] Ali H, Van Lier JE. Chem Rev 1999;99:2379−450.

[9] Boyle RW, Leznoff CC, Van Lier JE. Br J Cancer 1993;67:1177−81.

[10] Lever ABP, Hempstead MR, Leznoff CC, Liu W, Melnik M, Nevin WA, et al. Pure Appl Chem 1986;58:1467−76.

[11] Clarckson GJ, McKeown NB, Treacher KE. J Chem Soc Perkin Trans 1 1995:1817−23.

[12] Duro JA, Torre de la G, Barbera J, Serrano JL, Torres T. Chem Mater 1996;8:1061−6.

[13] Kalkan A, Bayır ZA. Monatsh Chem 2003;134:1555−60.

[14] Uslu RZ, Gül A. Mol Inorg Chem 2000;3:643−8.

[15] Hamuryudan E, Bayır ZA, Bekaroğlu Ö. Dyes Pigments 1999;43:77−81.

[16] Calvete M, Hanack M. Eur J Org Chem 2003;11:2080−3.

[17] Bayır ZA, Hamuryudan E, Gürek AG, Bekaroğlu Ö. J Porphyrins Phthalocyanines 1997;1:349−53.

[18] Öztürk R, Güner S, Aktaş B, Gül A. Supramol Chem 2005;17(3):233−41.

[19] Dinçer HA, Gül A, Koçak MB. J Porphyrins Phthalocyanines 2004;8:1204−8.

[20] Choi CF, Tsang PT, Huang JD, Chan EYM, Ko WH, Fong WP, et al. Chem Commun 2004:2236−7.

[21] Liu W, Jensen TJ, Fronczeh FR, Hammer RP, Smith KM, Vicente MGH. J Med Chem 2005;48:1033−41.

[22] Bayır ZA. Dyes Pigments 2005;65:235−42.

[23] Komatsu T, Ohta K, Fujimoto T, Yamamoto I. J Mater Chem 1994;4:533−6.

[24] Van der Pol JF, Neeleman E, Zwikker JW, Nolte RJM, Drenth W, Aerts J, et al. Liq Cryst 1989;6:577−92.

[25] Guillon D, Skoulios A, Piechoki C, Simon J, Weber P. Mol Cryst Liq Cryst 1983;100:275−84.

[26] Sirlin C, Bosio L, Simon J, Ahsen V, Yılmazer E, Bekaroğlu Ö. Chem Phys Lett 1987;139:362−4.

[27] Golcuk K, Altun A, Güner S, Kumru M, Aktas B. Spectrochim Acta Part A 2006;60:303−9.

[28] Weil JA, Bolton JR, Wertz JE. Electron paramagnetic resonance. New York: John Wiley and Sons Inc.; 1994.

[29] Güner S, Scedil;ener MK, Dinçer H, Köseoğlu Y, Kazan S, Koçak MB. J Magn Magn Mater 2006;300:530−3.

[30] Orti E, Bredas JL. J Chem Phys 1988;89:1009−16.

[31] Berezin BD. Coordination compounds of porphyrins and phthalocyanines. NY−Toronto: John Wiley; 1981.

[32] Hamuryudan E, Merey Ş, Bayır ZA. Dyes Pigments 2003;59:263−8.

[33] Bayır ZA, Merey Ş, Hamuryudan E. Monatsh Chem 2003;134:1027−31.

[34] Özkaya AR, Hamuryudan E, Bayır ZA, Bekaroğlu Ö. J Porphyrins Phthalocyanines 2000;4:689−97.

[35] Kalkan A, Koca A, Bayır ZA. Polyhedron 2004;23:3155−62.

[36] Gürsoy S, Bayır ZA, Hamuryudan E, Bekaroğlu Ö. Monatsh Chem 2000;131:287−92.

[37] Perrin DD, Armarego WLF. Purification of laboratory chemicals. 2nd ed. Oxford: Pergamon; 1980.

[38] Young JG, Onyebuagu W. J Org Chem 1990;55:2155−9.

[39] Kalkan A, Bayır ZA. Polyhedron 2006;25:39−42.

[40] Bayır ZA, Hamuryudan E, Bekaroğlu Ö. J Chem Res 1999:702−3.

[41] Arslanoğlu Y, Sevim AM, Hamuryudan E, Gül A. Dyes Pigments 2006;68:129−32.

[42] Heucher R, Chandramouli GVR, Manoharan PT. J Porphyrins Phthalocyanines 1998;2:423−7.