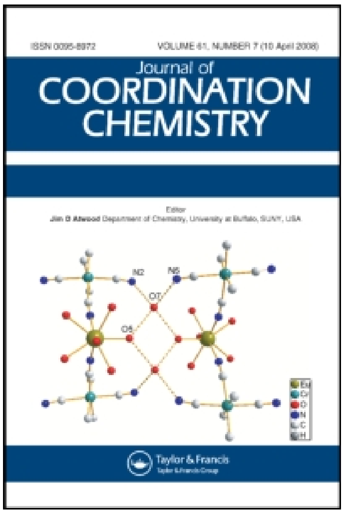


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization and electrochemical properties of copper(II) complexes with novel bidentate salicylaldimines derived from 3,5-di-*t*-butyl-2-hydroxybenzaldehyde

Esref Tas[a]; Mehmet Aslanoglu[a]; Mehmet Guler[a]; Mahmut Ulusoy[a]
[a] Department of Chemistry, Harran University, Sanliurfa, Turkey

To cite this Article Tas, Esref , Aslanoglu, Mehmet , Guler, Mehmet and Ulusoy, Mahmut(2004) 'Synthesis, characterization and electrochemical properties of copper(II) complexes with novel bidentate salicylaldimines derived from 3,5-di-*t*-butyl-2-hydroxybenzaldehyde', Journal of Coordination Chemistry, 57: 7, 583 — 589

To link to this Article: DOI: 10.1080/00958970410001697239

URL: http://dx.doi.org/10.1080/00958970410001697239

J. Coord. Chem., Vol. 57, No. 7, 10 May 2004, pp. 583–589

Taylor & Francis
Taylor & Francis Group

SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL PROPERTIES OF COPPER(II) COMPLEXES WITH NOVEL BIDENTATE SALICYLALDIMINES DERIVED FROM 3,5-DI-*t*-BUTYL-2-HYDROXYBENZALDEHYDE

ESREF TAS*, MEHMET ASLANOGLU,
MEHMET GULER and MAHMUT ULUSOY

Department of Chemistry, Harran University, Sanliurfa, Turkey

(Received 24 April 2003; Revised 6 October 2003; In final form 9 March 2004)

Mononuclear copper(II) complexes of novel bidentate salicylaldimines (L_xH) have been synthesized by the addition of $Cu(Ac)_2 \cdot 2H_2O$ to a mixture of 3,5-di-*t*-butyl-2-hydroxybenzaldehyde (3,5-DTB) and biologically active amines, 4-(3-aminopropyl)morpholine, 1-(3-aminopropyl)-2-pyrrolidinone and 1-(3-aminopropyl)-2-methylpiperidine. In this study *N*-[1-(3-aminopropyl)imidazole]-3,5-di-*t*-butylsalicylaldimine (L_1H) was synthesized by reaction of 3,5-DTB and 1-(3-aminopropyl)imidazole followed by complexation with copper(II). The complexes were characterized by FTIR, UV–VIS, ESR, MS, ^1H and ^{13}C NMR spectroscopy, magnetic susceptibility measurements and thermogravimetric analysis (TGA) and also by electrochemistry. The room-temperature powder ESR spectra of these complexes are similar and exhibit axially symmetric g-tensor parameters with $g_\parallel > g_\perp > g_e$ suggesting that the copper(II) atom has a $d_{x^2-y^2}$ ground state characteristic of square-planar or square-pyramidal stereochemistry. Thermal analysis indicated that $Cu(L_3)_2$ had the highest thermal stability of the complexes and $Cu(L_2)_2$ the lowest. Cyclic voltammetric experiments showed that all of the Cu(II) complexes underwent one-electron transfer, mainly diffusion controlled, as indicated by the dependence of the peak current on the square root of the scan rate.

Keywords: Sterically hindered salicylaldimine; Copper(II) complexes; Spectroscopy; Thermal stability; Cyclic voltammetry; Electrochemical properties

INTRODUCTION

Intramolecular electron transfer is a fundamental chemical phenomenon and relates specifically to redox processes that occur in both natural and synthetic electron-transfer systems [1]. The ability of metal ions to control the oxidation potentials of organic molecules by complexation plays a significant role in biological electron-transfer processes, molecular electronics and also in catalysis [2]. Copper(II) ions play a vital

---

*Corresponding author. E-mail: etas@harran.edu.tr

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970410001697239

role in biological redox metalloenzymes, including plastocyanin, hemocyanin, azurin, galactose oxidase and others [3–5]. Transition metal complexes with redox active ligands bearing sterically hindered salicylaldimines are reported to undergo one- or two-electron transfer [6]. Sterically hindered ligands bearing salicylaldimines are known to be effective antioxidants and are widely used in rancidification of fats and oils [6]. The thermal stability and the electron-transfer processes of such metal complexes with sterically hindered salicylaldimines are not well understood. Here we report the synthesis, stereochemical properties and stability of novel salicylaldimine complexes of copper(II) as well as their electrochemical properties.

EXPERIMENTAL

All chemicals were of analytical reagent grade and purchased from Sigma or Merck unless stated otherwise. 3,5-Di-*t*-butyl-2-hydroxybenzaldehyde (3,5-DTB) was synthesized according to the literature procedure [7]. 1-(3-Aminopropyl)imidazole, 4-(3-aminopropyl)morpholine, 1-(3-aminopropyl)-2-pyrrolidinone and 1-(3-aminopropyl)-2-methylpiperidine were purchased from Aldrich and used without purification. Tetrabutylammoniumtetrafluoroborate (TBATFB) was used as supporting electrolyte.

The elemental analyses were carried out in the laboratory of Tubitak (Turkish Scientific and Technical Research Council). IR spectra were recorded on a Perkin-Elmer RXI FTIR spectrometer as KBr pellets, ^{13}C and ^{1}H NMR spectra were recorded on a Varian XL-200 and magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature (20°C) using $Hg[Co(SCN)_4]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants [8]. UV spectra were recorded on a Schimadzu 1601 PC, thermogravimetric curves were recorded on a Seteram Labsys TG-16 thermobalance, and ESR spectra were recorded on a Varian Model E109C spectrometer in X-band with 100 kHz modulation frequency. The *g*-values were determined by comparison with a diphenylpicrylhydrazil (DPPH) sample of $g = 2.0037$. Mass spectra were recorded on Thermo Quest Auto Mass. Voltammetric experiments were performed using a Chemie Autolab potentiostat −12 with electrochemical software GPES 4.9. A three-electrode system was used: a 2-mm Pt-disc working electrode, an Ag/AgCl reference electrode and a Pt-wire counterelectrode. The working electrode was polished with 0.05-μm alumina prior to each experiment. Throughout the experiment oxygen-free nitrogen was bubbled through the solution for 10 min. Voltammetric experiments were performed at room temperature.

Synthesis of *N*-[1-(3-Aminopropyl)imidazole]-3,5-di-*t*-butylsalicylaldimine (L_1H)

L_1H was synthesized by the reaction of 5 mmol 3,5-DTB in 20 ml absolute ethanol and 5 mmol 1-(3-aminopropyl)imidazole in 10 ml ethanol, with the addition of 3–4 drops of acetic acid. The mixture was maintained at reflux for 120 min and then cooled to room temperature. Then 30 ml of *n*-hexane were added to precipitate the compound. After 2 days of refrigeration at 3–5°C, 1.023 g of product (60% yield) was obtained. The crystals were filtered in vacuum (mp 102°C). The product was soluble in common solvents such as CH_2Cl_2, $CHCl_3$, acetone, THF, C_2H_5OH and DMSO. Mass spectrum (EI): $m/z = 341$ $[M]^+$. Characteristic ^{13}C NMR bands of L_1H ($CDCl_3$, TMS, δ ppm):

C_1(127.16), C_2(125.9), C_3(136.61), C_4(44.18), C_5(34.94), C_6(55.62), C_7(167.09), C_8(129.66), C_9(157.78), C_{10}(117.53), C_{11}(137.09), C_{12}(118.61), C_{13}(140.23), C_{14}(31.73), C_{15}(29.30), C_{16}(34.047), C_{17}(31.39). Characteristic ^{1}H NMR bands of L_1H ($CDCl_3$, TMS, δ ppm): 1.31 [s, ($-^{17}CH_3$) 9H], 1.45 [s, ($-^{15}CH_3$) 9H], 2.1–2.2 [m, ($-^5CH_2$) 2H], 3.53 [t, ($-^4CH_2$) 2H], 4.04–4.07 [t, ($-^6CH_2$) 2H], 8.35 [s, ($-N{=}^7CH-$) 1H], 13.5 [s, ($-OH$) 1H], 7.41 [d, ($-^1CH{=}^2CH-$) 2H], 6.94 [s, ($-N{=}^3CH-N$) 1H]. Aromatic protons were observed at 7.09 ppm, s.

Synthesis of $Cu(L_1)_2$ Metal Complexes

L_1H (2 mmol) was dissolved in 30 ml absolute methanol and mixed with 1 mmol $Cu(Ac)_2 \cdot H_2O$ in 10 ml methanol. The stirred mixture was refluxed for 60 min. The volume was reduced to 15–20 ml and left to cool to room temperature. The compound was precipitated, filtered and washed with a small amount of methanol. The product was recrystallized in methanol. Yield: 64%, mp 228°C. The product was soluble in $CHCl_3$ and DMSO.

Synthesis of $Cu(L_x)_2$ Metal Complexes

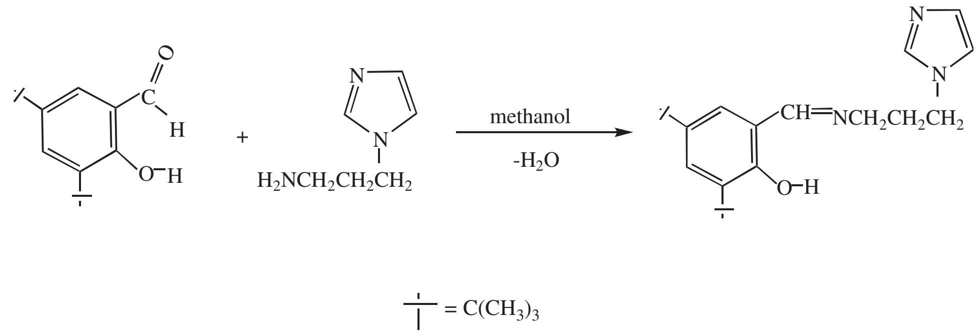
3,5-DTB (3 mmol) was dissolved in 30 ml methanol and mixed with 3 mmol of an amine compound [4-(3-aminopropyl)morpholine, 1-(3-aminopropyl)-2-pyrrolidinone or 1-(3-aminopropyl)-2-methylpiperidine] in 20 ml methanol. The stirred mixture was refluxed and a solution of copper(II) acetate monohydrate (1.5 mmol) in 10 ml methanol was added. The mixture was heated at 60–65°C with stirring for about 60 min and evaporated to a volume of 15–20 ml and left to cool to room temperature. The precipitated complex was filtered and washed with a small amount of methanol. The products were soluble in $CHCl_3$ and DMSO.

RESULTS AND DISCUSSION

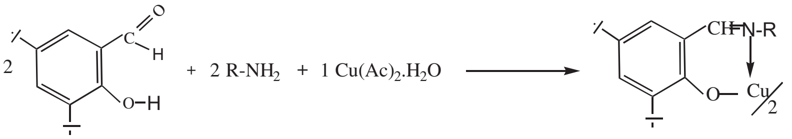
The analytical data are presented in Table I. The synthetic route to the Schiff-base ligand (L_1H) is shown in Scheme 1. Condensation of 3,5-DTB with 1-(3-aminopropyl)-imidazole, 4-(3-aminopropyl)morpholine, 1-(3-aminopropyl)-2-pyrrolidinone and

TABLE I The colours, formulas, formula weights, melting points, magnetic susceptibilities, yields and elemental analyses results for the ligand and the complexes

Compound	*FW (g mol^{-1})*	*Colour*	*mp (°C(dec.))*	*Yield (%)*	*μ_{eff} (BM)*	*Elemental analyses % calculated (found)*		
						C	*H*	*N*
L_1H $C_{21}H_{30}N_3O$	341	Yellow	102	60	–	73.9 (74.3)	8.79 (8.35)	12.31 (12.4)
$Cu(L_1)_2$ $C_{42}H_{58}N_6O_2Cu$	743.54	Dark green	228	64	2.06	67.78 (67.37)	7.80 (7.58)	11.29 (11.32)
$Cu(L_2)_2$ $C_{44}H_{70}N_4O_4Cu$	783	Green	175.5	59	1.85	67.41 (67.86)	8.94 (8.71)	7.15 (6.97)
$Cu(L_3)_2$ $C_{44}H_{66}N_4O_4Cu$	778	Dark brown	170	70	1.98	67.81 (68.57)	8.48 (7.95)	7.19 (6.86)
$Cu(L_4)_2$ $C_{48}H_{78}N_4O_2Cu$	806	Dark brown	171	65	2.10	71.39 (71.38)	9.66 (9.28)	6.94 (6.95)



SCHEME 1 Synthetic route to the Schiff base (L_1H).



SCHEME 2 $Cu(L_x)_2$ complexes. R = 4-(3-aminopropyl)morpholine, 1-(3-aminopropyl)-2-pyrrolidinone, 1-(3-aminopropyl)-2-methylpiperidine.

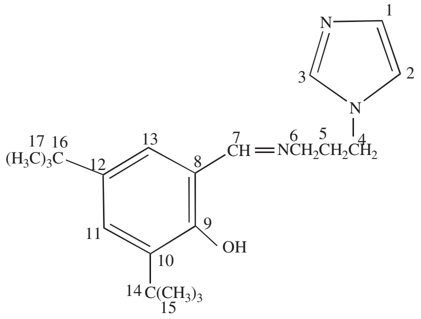


FIGURE 1 The structure of the ligand L_1H.

1-(3-aminopropyl)-2-methylpiperidine produced the $Cu(L_x)_2$ complexes as shown in Scheme 2.

Electron-impact mass spectrometric data for L_1H show a molecular ion peak $m/z = 341$, in agreement with the proposed structure as shown in Fig. 1. This structure is also in accordance with the elemental analyses, IR, ^1H and ^{13}C NMR spectral data. In the ^1H NMR spectra, the chemical shift of the Ar–OH proton is observed at 13.5(s) ppm. This chemical shift disappeared upon addition of D_2O to the solution. The chemical shift of the CH=N proton is observed at 8.3 ppm.

Spectral data for L_1H and $Cu(L_x)_2$ are presented in Table II. A strong band observed in the IR spectra of the free ligand at 1626 cm^{-1}, which is attributed to the C=N stretch, showed a negative shift to *ca* 1615–1620 cm^{-1} in the spectra of all the complexes, indicating coordination of the azomethine nitrogen atom to copper [9–13].

TABLE II IR and electronic spectral data for L_1H, $Cu(L_1)_2$ and $Cu(L_x)_2$ complexes

Compound	*IR spectra (cm^{-1})*		*Electronic spectra (λ/nm)*					
	νO–H	*νC=N*						
L_1H_1	3410	1626	220	260	330	410		
$Cu(L_1)_2$	–	1620	247	280sh	325	407	646	
$Cu(L_2)_2$	–	1615	267	334	385	634		
$Cu(L_3)_2$	–	1619	261	330	382	401	650sh	
$Cu(L_4)_2$	–	1620	272	329	385	406	480sh	650

sh, shoulder.

TABLE III ESR spectral data for $Cu(L_1)_2$ and $Cu(L_x)_2$ complexes

Compound	*Solid-state spectra*			*Solution spectra*	
	$g_\parallel$	$g_\perp$	g_{uv}	g_{iso}	$A_{iso(G)}$
$Cu(L_1)_2$	2.159	2.052	2.088	–	–
$Cu(L_2)_2$	2.082	2.037	2.052	2.124	76
$Cu(L_3)_2$	2.098	2.032	2.054	2.116	72

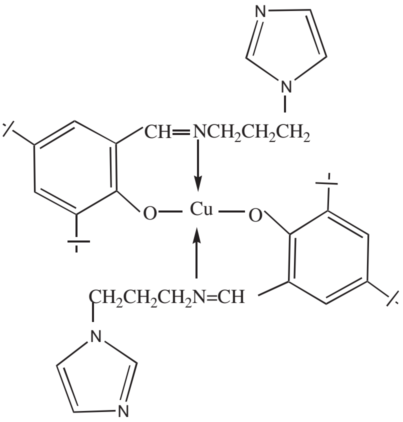


FIGURE 2 The structure of $Cu(L_1)_2$.

The ESR spectra of polycrystalline samples of $Cu(L_2)_2$ and $Cu(L_3)_2$ recorded at 300 K did not show $^{63.65}$Cu hyperfine splitting in the g_z region, and no half-field signals associated with $\Delta m_s = \pm 2$ forbidden transitions were observed. The room temperature powder ESR spectra of these complexes are similar and exhibit axially symmetric g-tensor parameters with $g_\parallel > g_\perp > g_e$ (Table III), indicating that the copper(II) atom has a $d_{x^2-y^2}$ ground-state characteristic of square-planar or square-pyramidal stereochemistry [14,15].

The ESR spectra of $Cu(L_2)_2$ and $Cu(L_3)_2$ in $CHCl_3$ solution at 300 K showed typical four-line patterns with $g_{iso} = 2.174$, $A^{Cu}_{iso} = 76G$ and $g_{iso} = 2.116$, $A^{Cu}_{iso} = 72G$, without any additional superhyperfine splitting due to coordinated nitrogens ^{14}N ($I = 1$). The ESR spectrum of $Cu(L_1)_2$ in $CHCl_3$ at 300 K shows an unusual poorly resolved, broad signal centred at $g = 2.092$. The observed broadening of the ESR line widths probably arises from intermolecular dipole–dipole interactions between paramagnetic copper ions.

In the electronic spectrum of the Schiff-base ligand L_1H, recorded in ethanol solution, the aromatic bands at 220–230 nm are attributed to a benzene $\pi \rightarrow \pi^*$ transition. The band at 410 nm is assigned to the imino $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transition [16].

The electronic spectra of the complexes were recorded in chloroform as solvent. The bands below 420 nm have very high extinction coefficients and are almost certainly associated with intraligand $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ or charge-transfer transitions. The electronic spectra of the Cu(II) complexes show an absorption band at 634–650 nm attributed to the $^2T_{2g} \rightarrow {}^2E_g$ (G) transition, which are compatible with these complexes having a square-planar structure [17, 18] (Table II).

The compounds were also investigated by TGA. The TGA curves, which were obtained under nitrogen at 20–900°C, show that ligand L_1H and $Cu(L_1)_2$, $Cu(L_2)_2$, $Cu(L_3)_2$ and $Cu(L_4)_2$ complexes are thermally stable up to 294, 250, 221, 267 and 262°C, respectively. Thus $Cu(L_3)_2$ has the highest thermal stability of the complexes and $Cu(L_2)_2$ the lowest.

A typical cyclic voltammogram of $Cu(L_4)_2$ in DMSO containing 0.1 M TBATFB is shown in Fig. 3. The cyclic voltammetric data for the copper(II) complexes are given in Table IV. The peak separation values of the complexes varied between 160 and

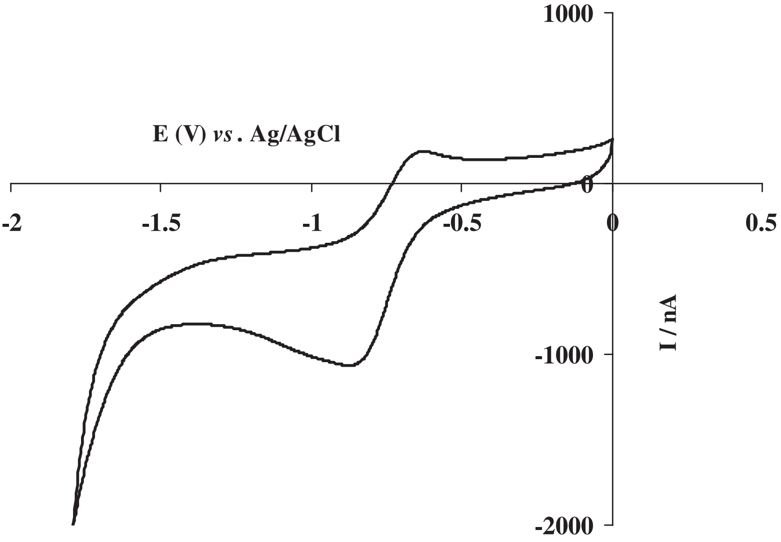


FIGURE 3 A cyclic voltammogram of 1×10^{-4} M $Cu(L_4)_2$ in DMSO containing 0.1 M TBATFB as supporting electrolyte. Scan rate = 0.1 V s^{-1}, Equilibrium time = 10 s.

TABLE IV Voltammetric data for copper(II) complexes in DMSO

Complex	*Epa (V)*	*Epc (V)*	*ΔEp (V)*	$E_{1/2}$
$Cu(L_2)_2$	–0.62	–0.85	0.23	0.735
$Cu(L_3)_2$	–0.61	–0.87	0.26	0.740
$Cu(L_4)_2$	–0.63	–0.86	0.23	0.745
$Cu(L_5)_2$	–0.65	–0.81	0.16	0.730

Supporting electrolyte = 0.1 M TBATFB; scan rate = 0.1 V s^{-1}; equilibrium time = 10 s.

260 mV, indicating that the copper(II) complexes undergo a single one-electron quasi-reversible oxidation/reduction reaction, which is attributed to Cu(II)/Cu(I) species. The electrochemical processes of all of the copper(II) complexes retain their quasi-reversible character even at a scan rate of 250 mV s^{-1}. There is a linear relationship between the peak current and the square root of the scan rate at 10–250 mV s^{-1} in DMSO, indicating that the electrochemical process is diffusion controlled [19].

Acknowledgments

Financial support from the Research Fund of Harran University (Project No. 343) is greatly appreciated and we are grateful to Professor V. T. Kasumov for helpful discussions on the ESR spectra.

References

[1] R.A. Sheldon and J.R. Kochi, *Metal Catalysed Oxidation of Organic Compounds* (Academic Press, New York, 1981).
[2] (a) W. Kaim, *Coord. Chem. Rev.* **76**, 187 (1987); (b) T.J. Meyer, *Acc. Chem. Res.* **11**, 94 (1978); (c) D.E. Richardson and H. Taube, *Coord. Chem. Rev.* **60**, 107 (1984); (d) J.R. Reimers and N.S. Hush (Eds.), *Electron Transfer in Biology and the Solid State* (American Chemical Society, Washington, DC, 1990).
[3] (a) M.M. Whittaker, In: K.D. Karlin and Z. Tyeklar (Eds.), *Bioinorganic Chemistry of Copper* (Chapman & Hall, New York, 1993); (b) J.A. Halfen, V.G. Toung and W.B. Tolman, *Angew. Chem., Int. Ed. Engl.* **35**, 1687 (1996).
[4] (a) E.I. Solomon, U.M. Sundaram and T.E. Makonkin, *Chem. Rev.* **96**, 2563 (1996); (b) R. Huber, *Angew. Chem., Int. Ed. Engl.* **28**, 848 (1989); (c) D. Mansuy, *Pure Appl. Chem.* **59**, 759 (1997).
[5] (a) O. Kahn, *Angew. Chem., Int. Ed. Engl.* **24**, 834 (1985); (b) J.P. Klinman, *Chem. Rev.* **96**, 2541 (1996).
[6] D. Zurita, S. Menage, J.L. Pierre and E.S. Aman, *J. Biol. Inorg. Chem.* **2**, 46 (1997).
[7] J.F. Larrow, E.N. Jacobsen, Y. Gao, Y. Hong, X. Nie and C.M. Zepp, *J. Org. Chem.* **59**, 1939 (1994).
[8] A. Earnshaw, *Introduction to Magnetochemistry* (Academic Press, London, 1986), p. 4.
[9] M. Şekerci, C. Alkan, A. Çukurovalı and S. Saydam, *XIIth National Chemistry Congress*, Edirne, Turkey (1998), p. 196.
[10] M. Köksal, M. Tümer and S. Serin, *Synth. React. Inorg. Met.-Org. Chem.* **26**, 1577 (1996).
[11] M. Tümer, M. Köksal and S. Serin, *Synth. React. Inorg. Met.-Org. Chem.* **27**, 775 (1997).
[12] B.S. Garg, P.K. Singh and J.L. Sharma, *Synth. React. Inorg. Met.-Org. Chem.* **30**, 803 (2000).
[13] E. Taş, V.T. Kasumov, Ö. Sahin and M. Özdemir, *Transition Metal Chem.* **27**, 442 (2002).
[14] B.Y. Hathaway and D.E. Billing, *Coord. Chem. Rev.* **5**, 143 (1970).
[15] G. Speier, Y. Csihony, A.M. Whaten and C.G. Pizpont, *Inorg. Chem.* **35**, 3519 (1996).
[16] H. Temel and M. Sekerci, *Synth. React. Inorg. Met.-Org. Chem.* **31**, 849 (2001).
[17] S. Tabassum, A. Bashar, F. Arjmand and K.S. Siddigi, *Synth. React. Inorg. Met.-Org. Chem.* **27**, 487 (1997).
[18] V.T. Kasumov, *Transition Metal Chem.* **27**, 228 (2002).
[19] A.J. Bard and L.R. Faulkner (Eds.), *Electrochemical Methods: Fundamentals and Applications* (Wiley, New York, 2001), 2nd Edn.