Polish J. Chem., **78**, 903–909 (2004) **INORGANIC CHEMISTRY**

Synthesis, Characterization and Electrochemical Studies of Nickel(II) and Cobalt(II) Complexes with Novel Bidentate Salicylaldimines

by E. Tas[*], M. Aslanoglu, M. Ulusoy and M. Guler

Department of Chemistry, Harran University, 63100 Sanliurfa, Turkey

(Received December 23rd, 2003; revised manuscript March 4th, 2004)

Several mononuclear Ni(II) and Co(II) complexes of bidentate salicylaldimines (L_xH), derived from 3,5-di-tert-butyl-2-hydroxybenzaldehyde with biologically active amines [1-(3-aminopropyl)imidazole, 4-(3-aminopropyl)morpholine, 1-(3-aminopropyl)-2-pyrrolidinone], have been synthesized. The complexes have been characterized by FT-IR, UV-vis, MS, ^{1}H-NMR and ^{13}C-NMR, magnetic susceptibility measurements, thermogravimetric analyses (TGA) and electrochemistry. As a result of thermal analyses, $Co(L_3)_2$ has highest thermal stability of the complexes, whereas the smallest one has $Ni(L_2)_2$. Electrochemical experiments indicated that Ni(II) and Co(II) complexes show quasi reversible reduction to Ni(I) and Co(I), respectively.

Key words: Schiff base, cobalt(II), nickel(II) complexes, synthesis, redox properties

There is a growing interest in the synthesis of Schiff bases and their metal complexes because of their biochemical, analytical, industrial and therapeutic applications [1,2]. The ability of Schiff bases to form stable complexes with transition metal ions has spurred interest in such compounds.

Intra-molecular electron transfer is a fundamental chemical phenomenon and relates specifically to redox processes which occur in both natural and synthetic electron-transfer systems [3]. The ability of metal ions to control the oxidation potentials of organic molecules by complexation has a significant role in biological electron-transfer processes, molecular electronics and also in catalysis [4]. The nickel(II) ions play a central role in biological redox metalloenzymes like plastocyanin, hemocyanin, azurin, galactose oxidase and others [5–7]. It has been reported that transition metal complexes with redox active ligands bearing sterically hindered salicylaldimines undergo one or two electron transfer [8]. It is also known that sterically hindered ligands bearing salicylaldimines are effective antioxidants and are widely used in rancidification of fats and oils [8]. However, the electron transfer processes of such metal complexes with sterically hindered salicylaldimines are not well understood.

In the present paper, we report the synthesis, spectroscopic characterization of novel salicylaldimine complexes of Ni(II) and Co(II) as well as their electrochemical properties.

---

[*] Author for correspondence

EXPERIMENTAL

3,5-Di-tert-butyl-2-hydroxybenzaldehyde (3,5-DTB) was synthesized according to the literature procedure [8]. 1-(3-Aminopropyl)imidazole, 4-(3-aminopropyl)morpholine and 1-(3-aminopropyl)-2-pyrrolidinone were purchased from Aldrich. Tetrabutylammonium tetrafluoroborate (TBATFB) (Fluka) was used as supporting electrolyte in voltammetric studies.

The elemental analyses were carried out in the Laboratory of the Scientific and Technical Research Council of Turkey (TUBITAK). IR spectra were recorded on a Perkin Elmer Spectrum RXI FT-IR Spectrometer as KBr pellets, while ^{13}C and ^{1}H NMR spectra were recorded on a Varian XL-200. 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 [9]. UV spectra were recorded on a Schimadzu 1601 PC and thermogravimetric (TGA) curves were recorded on a Seteram Labsys TG-16 thermobalance. Mass spectra were recorded on Thermo Quest Auto Mass. Voltammetric experiments were performed using an EcoChemie Autolab potentiostat-12 with an electrochemical software GPES 4.9. A three electrode system was used: a 2 mm size Pt disc working electrode, an Ag/AgCl reference electrode and a Pt wire counter electrode. 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.

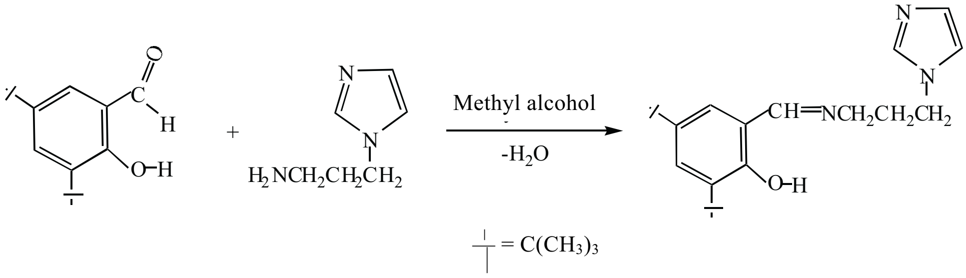
Synthesis of N-(1-(3-aminopropyl)imidazole)-3,5-di-t-butylsalicylaldimine (L_1H): N-(1-(3-aminopropyl)imidazole)-3,5-di-t-butylsalicylaldimine (L_1H) ligand was synthesized by the reaction of 5 mmol 3,5-di-tert–butyl-2-hydroxybenzaldehyde in 20 ml absolute ethanol and 5 mmol 1-(3-aminopropyl)imidazole in 10 ml ethanol. Also 3–4 drops of acetic acid were added. The mixture was maintained at reflux for 120 min. followed by cooling to room temperature. Then 30 ml of n-hexane was 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 (m.p. 102°C). The product is 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_{16}(34.047), C_{14}(31.73), C_{17}(31.39), C_{15}(29.30). Characteristic ^{1}H NMR bands of L_1H ($CDCl_3$, TMS, δ ppm): 1.31 [s, $(-^{17}C\underline{H}_3)$ 9H], 1.45 [s, $(-^{15}C\underline{H}_3)$ 9H], 2.1–2.2 [m, $(-^{5}C\underline{H}_2)$ 2H], 3.53 [t, $(-^{4}CH_2)$ 2H], 4.04–4.07 [t, $(-^{6}CH_2)$ 2H], 8.35 [s, $(-N{=}^{7}C\underline{H}-)$ 1H], 13.5 [s, $(-O\underline{H})$ 1H], 7.41 [d, $(-^{1}C\underline{H}{=}^{2}C\underline{H}-)$ 2H], 6.94 [s, $(-N{=}^{3}C\underline{H}-N)$ 1H]. Aromatic protons were observed 7.09 ppm, s. Elemental analysis for $C_{21}H_{30}N_3O$ (MW 341.00): Calculated (%): C, 73.90; H, 8.79; N, 12.31. Found (%): C, 74.30; H, 8.35; N, 12.40.

Synthesis of $Ni(L_1)_2$ and $Co(L_1)_2$ metal complexes: 2 mmol L_1H was dissolved in 30 mL of absolute methanol and 1 mmol $Ni(Ac)_2 \cdot 4H_2O$ or $Co(Ac)_2 \cdot 4H_2O$ in 10 mL methanol were mixed. The stirred mixture was refluxed for 60 min. The mixture was evaporated to 15–20 mL left to cool to room temperature. The compound was precipitated, washed with a small amount of methanol/H_2O (1:1) and filtered in vacuum. The products are soluble in solvents such as $CHCl_3$ and DMSO. The results of elemental analyses for $C_{42}H_{58}N_6O_2Ni$ (MW 738.70): Calculated (%): C, 68.23; H, 7.85; N, 11.37. Found (%): C, 68.48; H, 7.88; N, 11.63 and for $C_{42}H_{58}N_6O_2Co$ (MW 738.90): Calculated (%): C, 68.20; H, 7.85; N, 11.36. Found (%): C, 68.45; H, 7.64; N, 11.00.

Synthesis of $Ni(L_{2,3})_2$ and $Co(L_{2,3})_2$ metal complexes: (3 mmol) 3,5-di-tert-butyl-2-hydroxybenzaldehyde was dissolved in 30 mL methanol and (3 mmol) amine compounds [4-(3-aminopropyl)morpholine and 1-(3-aminopropyl)-2-pyrrolidinone in 20 mL methanol were mixed. The stirred mixture was refluxed. Solution of nickel(II) or cobalt(II) acetate (1.5 mmol) in 10 mL methanol was added. The mixture was heated at 60–65°C with stirring for about 60 min. evaporated to 15–20 mL and left to cool to room temperature. The precipitated complex was filtered, washed with a small amount of methanol. The products are soluble in solvents such as $CHCl_3$ and DMSO. The results of elemental analyses for $C_{44}H_{70}N_4O_4Ni$ (MW 778.16): Calculated (%): C, 67.85; H, 8.99; N, 7.19. Found (%): C, 67.83; H, 8.81; N, 7.49; for $C_{44}H_{66}N_4O_4Ni$ (MW 773.16): Calculated (%): C, 68.29; H, 8.53; N, 7.24. Found (%): C, 68.40; H, 8.61; N, 7.11; for $C_{44}H_{70}N_4O_4Co$ (MW 778.36): Calculated (%): C, 67.83; H, 8.99; N, 7.19. Found (%): C, 68.03; H, 8.76; N, 7.41; for $C_{44}H_{66}N_4O_4Co$ (MW 773.36): Calculated (%): C, 68.27; H, 8.53; N, 7.24. Found (%): C, 68.53; H, 8.51; N, 7.15.

RESULTS AND DISCUSSION

The characteristics of the ligand L_1H and all complexes under investigation are presented in Table 1. The Schiff base ligand (L_1H) was prepared by condensation of 3,5-di-tert-butyl-2-hydroxybenzaldehyde and 1-(3-aminopropyl)imidazole, 4-(3-aminopropyl)morpholine, 1-(3-aminopropyl)-2-pyrrolidinone, in ethanol as shown in Scheme 1 and Scheme 2.



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

Table 1. The colors, formulas, formula weights, melting points, yields and results of magnetic susceptibilities of the ligands and the complexes.

Compounds	F.W. (g/mol)	Color	M.p.(dec.) °C	Yield (%)	μ_{eff} [B.M.]
L_1H $C_{21}H_{30}N_3O$	341.00	Yellow	102	60	–
$Ni(L_1)_2$ $C_{42}H_{58}N_6O_2Ni$	738.70	Dark Green	130	64	3.16
$Ni(L_2)_2$ $C_{44}H_{70}N_4O_4Ni$	778.16	Green	165	59	2.85
$Ni(L_3)_2$ $C_{44}H_{66}N_4O_4Ni$	773.16	Green	290	70	2.86
$Co(L_1)_2$ $C_{42}H_{58}N_6O_2Co$	738.90	Dark Brown	135	73	4.37
$Co(L_2)_2$ $C_{44}H_{70}N_4O_4Co$	778.36	Orange	197	65	3.81
$Co(L_3)_2$ $C_{44}H_{66}N_4O_4Co$	773.36	Brown	173	67	3.96

Table 2. IR and electronic spectral data for L_1H, $M(L_1)_2$ and $M(L_x)_2$ complexes.

Compounds	IR spectra (cm^{-1})		Electronic spectra, λ/nm					
	υO-H	υC=N						
L1H	3410	1626	220	260	330	410		
$Ni(L_1)_2$	–	1623	265	320	335	635	648	
$Ni(L_2)_2$	–	1618	240*	267	343	400*	634	
$Ni(L_3)_2$	–	1615	295	384	450*			
$Co(L_1)_2$	–	1625	265	380	590			
$Co(L_2)_2$	–	1623	246	266	361	400*	591	634
$Co(L_3)_2$	–	1605	273	333	390	460*	560	700

*Shoulder

Electron-impact mass spectrometric data show a molecular ion peak m/z = 341 in agreement with the structure of L_1H ligand shown in Scheme 1. The elemental analyses, IR, ^1H and ^{13}C-NMR spectral data also support the proposed structure of the compound L_1H.

In the ^1H-NMR spectra of L_1H, chemical shifts of Ar–OH proton is observed at 13.5 ppm as a singlet. This chemical shift disappears upon addition of D_2O to the solution. Also, chemical shift of CH=N proton is observed at 8.3 ppm.

The L_1H ligand was synthesized as mentioned in the experimental section. However, Ni(II) and Co(II) complexes of L_2H and L_3H were synthesized without obtaining the ligands (L_2H and L_3H) directly as shown in Scheme 2.

Characteristics of the IR and electronic spectra of L_1H, $Ni(L_x)_2$ and $Co(L_x)_2$ are presented in Table 2. A strong band observed in the IR spectra of the free ligand in 1626 cm^{-1} region, which is attributed to the C=N stretch, showed a negative shift to *ca.* 1605–1625 cm^{-1} in the spectra of all the complexes, indicating coordination of the azomethine nitrogen atom to nickel and cobalt [10–14].

In the electronic spectra of this ligand (L_1H) along with bands in the 220–230 nm region which are due to intra-ligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions involving molecular orbitals of the C=N chromophore and benzene ring, a broad shoulder around at 410 nm was observed. This absorption (in EtOH solutions) is attributed to the $n \rightarrow \pi^*$ transition of the dipolar ketoamine tautomeric structure of L_1H [14–16].

The electronic spectra of the complexes were examined in chloroform. The bands below 420 nm have very high extinction coefficients and are almost certainly associated with intra-ligand $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ or charge-transfer transitions [17]. In the complexes, the $\pi \rightarrow \pi^*$ transition is shifted to a longer wavelength as a consequence of coordination when binding with the metal, confirming the formation of Schiff base metal complexes [18]. The electronic spectrum of the Ni(II) complexes show absorption bands at *ca.* 600 nm $^3A_2(F) \rightarrow {}^3T_2(F)$ and at *ca.* 400 nm $^3A_2(F) \rightarrow {}^3T_1(F)$ transitions attributed to the tetrahedral geometry [19]. The electronic spectrum of the Co(II) complexes show absorption bands at 460–700 nm attributed to the $^4A_2 \rightarrow {}^4T_1(P)$ transition, which is compatible with these complexes having a tetrahedral structure [20],

Table 2. The magnetic moments of the mononuclear complexes of Co(II) and Ni(II) are 4.37–3.81 and 3.16–2.85 B.M., respectively. These results are comparable to the values reported for slightly distorted tetrahedral geometry [21]. The structures of the complexes are given in Figure 1. The results of elemental analyses support the structures of L_1H and all other complexes.

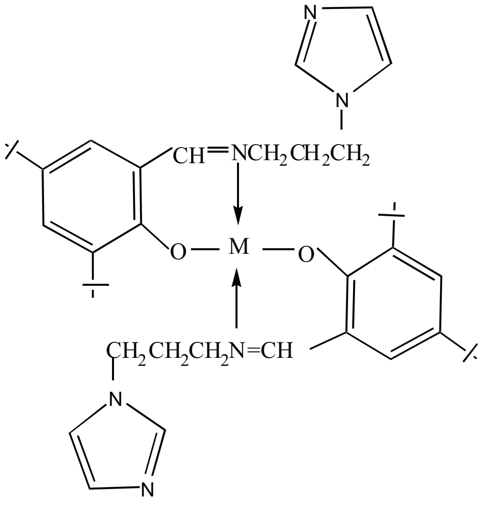
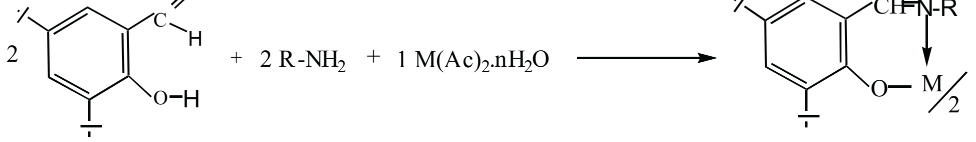


Figure 1. The structures of the $Ni(L_1)_2$ and $Co(L_1)_2$ complexes [M = Ni(II) and Co(II)].

The thermal studies were carried out by using TGA. The TGA curves, which were obtained in nitrogen atmosphere between 20–900°C, show that ligand (L_1H) and $Ni(L_1)_2$, $Co(L_2)_2$, $Ni(L_2)_2$ and $Co(L_3)_2$ complexes are thermally stable up to 294°C, 249°C, 230°C, 191°C and 265°C respectively. Results of thermal analyses show that $Co(L_3)_2$ has highest thermal stability of the all complexes, whereas the lowest one has $Ni(L_2)_2$.



R = 4-(3-aminopropyl)morpholine, 1-(3-aminopropyl)-2-pyrrolidinone [M = Ni(II) and Co(II)]

Scheme 2. Synthetic route to the $Ni(L_x)_2$ and $Co(L_x)_2$ complexes.

Table 3. Voltammetric data for Ni(II) and Co(II) complexes.

Complex	*Epa*(V)	*Epc*(V)	Δ*Ep*(V)
$Ni(L_1)_2$	–1.329	–1.453	0.124
$Ni(L_2)_2$	–1.402	–1.490	0.088
$Co(L_1)_2$	–0.620	–0.910	0.290
$Co(L_2)_2$	–0.640	–0.887	0.247
$Co(L_3)_2$	–0.500	–0.732	0.232

Supporting electrolyte = 0.1 M TBATFB. Scan rate = 0.1 Vs^{-1}. Equilibrium time = 10 s.

Table 3 shows the cyclic voltammetric data of 5×10^{-4} M of the Ni(II) and Co(II) complexes at sweep rates of 25 to 500 mVs^{-1} obtained at a Pt electrode in deoxygenated DMSO solution, with TBATFB as supporting electrolyte. The data revealed that both Ni(II) and Co(II) complexes undergo a single one-electron oxidation/reduction electrochemical processes. The one-electron reduction peak (*Epc*), corresponding to the Ni(II)/Ni(I) pairs, occurs in the potential range –1.453 to –1.490 mV, with a directly associated re-oxidation peak (*Epa*) in the reverse scan, whose potential values fall within the range –1.329 to –1.402 mV (Table 3). In Figure 2, this general electrochemical response is illustrated by the voltammogram of the complex, $Ni(L_2)_2$. In the case of cobalt complexes, the one-electron reduction peak (*Epc*), which is attributed to the Co(II)/Co(I) couple, occurs in the potential range –732 to –910 mV,

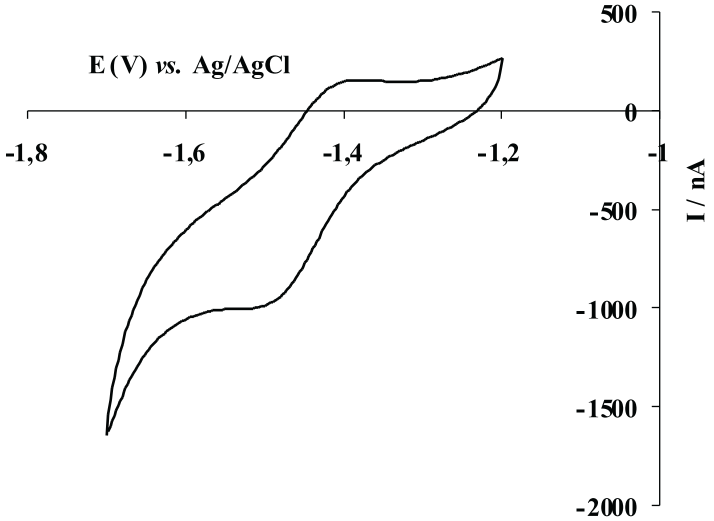


Figure 2. Cyclic voltammogram of 1×10^{-4} M $Ni(L_2)_2$ in DMSO containing 0.1 M TBATFB as supporting electrolyte. Scan rate = 0.1 Vs^{-1}, Equilibrium time = 10 s.

with a directly associated re-oxidation peak (*Epa*) in the reverse scan, whose potential values were within the range –500 to –640 mV. Analysis of the cyclic voltammetric responses to scan rates showed the following features: the anodic to cathodic peak current ratio (*Ipa*/*Ipc*) decreased at faster scan rates for all complexes; the difference between the potential of the anodic peak and that of the cathodic peak gradually increased going from 25 to 500 mVs^{-1}. These data are diagnostic for a simple quasi-reversible one-electron charge transfer [22].

Acknowledgment

The authors greatly appreciate the financial support from the Research Fund of Harran University (Project No: HUBAK-343).

REFERENCES

1. Herzfeld R. and Nagy P., *Spectrosc. Lett.,* **31**, 57 (1999).
2. Temel H., Ilhan S., Sekerci M. and Ziyadanogullari R., *Spectrosc. Lett.,* **35**, 219 (2002).
3. Sheldon R.A. and Kochi J.R., *Metal Catalysed Oxidation of Organic Compounds.* Academic Press, New York, (1981)
4. (a) Kaim W., *Coord. Chem. Rev.,* **76,** 187 (1987); (b) Meyer T.J., *Acc. Chem. Res.,* **11**, 94 (1978); (c) Richardson D.E. and Taube H., *Coord. Chem. Rev.,* **60**, 107 (1984); (d) Reimers J.R. and Hush N.S, (eds), *Electron Transfer in Biology and the Solid State*, Am. Chem. Soc., Washington, DC, 1990.
5. (a) Whittaker M.M., *In Bioinorganic Chemistry of Copper*, Karlin K.D. and Tyeklar Z., eds. Chapman & Hall, New York, London, 1993; (b) Halfen J.A., Toung V.G. and Tolman W.B., *Angew. Chem. Int. Ed. Engl.,* **35**, 1687 (1996).
6. (a) Solomon E.I., Sundaram U.M. and Makonkin T.E., *Chem. Rev.,* **96**, 2563 (1996); (b) Huber R., *Angew. Chem. Int. Ed. Engl.,* **28,** 848 (1989); (c) Mansuy D., *Pure Appl. Chem.,* **59**, 759 (1997).
7. (a) Kahn O., *Angew. Chem. Int. Ed. Engl.,* **24**, 834 (1985); (b) Klinman J.P., *Chem. Rev.,* **96**, 2541 *(*1996); (c) Zurita D., Menage S., Pierre J. L. and Aman E.S., *J. Biol. Inorg. Chem.,* **2**, 46 (1997).
8. Larrow J.F., Jacobsen E.N., Gao Y., Hong Y., Nie X. and Zepp C.M., *J. Org. Chem.,* **59**, 1939 (1994).
9. Earnshaw A., *Introduction to Magnetochemistry*, Academic Press, London, p. 4, 1968.
10. Ayad M.I., Salam S.A. and Mabrouk H.E., *Thermochim. Acta.,* **1**, 65 (1991).
11. Koksal M., Tumer M. and Serin S., *Synth. React. Inorg. Met–Org. Chem*., **26**(9), 1577 (1996).
12. Tumer M., Koksal M. and Serin S., *Synth. React. Inorg. Met–Org Chem.,* **27**(9), 775 (1997).
13. Garg B.S., Singh P.K. and Sharma J.L., *Synth. React. Inorg. Met–Org. Chem.,* **30**, 803 (2000).
14. Tas E., Kasumov V.T., Sahin O. and Ozdemir M., *Trans. Met. Chem.,* **27**, 442 (2002).
15. (a) Gerald O. and Dudek E.P., *J. Am. Chem. Soc.,* **88**, 2407 (1966); (b) Alexander P.W. and Sleet R.J., *Aust. J. Chem.,* **23**, 1183 (1970); (c) Seliskar C.J., *J. Phys. Chem.,* **81**, 1331 (1977).
16. Nishida Y. and Kida S., *Coord. Chem. Rev.,* **27**, 275 (1979).
17. (a) Kasumov V.T., *Trans. Met. Chem.,* **27**, 228 (2002); (b) Sheat S.V. and Waters T.N., *J. Inorg. Nucl. Chem.,* **26**, 1221 (1964).
18. Guangbin W., *Spectrosc. Lett.,* **32**(4), 1061 (1999).
19. (a) Everett G.W. and Holm R.H., *J. Am. Chem. Soc.,* **87**, 2117 (1965); (b) Sacconi L., Ciampolini M. and Nardi N., *J. Am. Chem. Soc.,* **86**, 819 (1964); (c) Holm R.H. and O'Connor M.J., *Prog. Inorg. Chem.,* **14**, 214 (1971).
20. Satpathy K.C., Mishra H.P. and Mishra R., *J. Inorg. Nucl. Chem.,* **43**(11), 2765 (1981).
21. (a) West B., *J. Chem. Soc.,* 3123 (1952); (b) Maurya R.C., Patel P. and Rajput S., *Synth. React. Inorg. Met–Org. Chem.,* **33**(5), 817 (2003).
22. Bard A.J. and Faulkner L.R., (Eds), *Electrochemical Methods: Fundamentals and Applications*, 2nd edn., Wiley, NY, 2001.