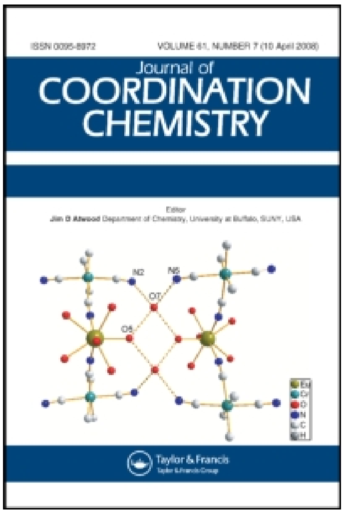

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R. M. Ramadan[a]; M. S. A. Hamza[a]; S. A. Alp[b]
[a] Department of Chemistry, Faculty of Science, Ain Shams University, Cairo, Egypt [b] Department of Chemistry, University College for Girls, Ain Shams University, Cairo, Egypt

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REACTIONS OF CHROMIUM AND MOLYBDENUM CARBONYLS WITH A QUADRIDENTATE SCHIFF BASE

R.M. RAMADAN[a],* M.S.A. HAMZA[a] and S.A. ALI[b],

[a]*Department of Chemistry, Faculty of Science, Ain Shams University, Cairo, Egypt;*
[b]*Department of Chemistry, University College for Girls, Ain Shams University, Cairo, Egypt*

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Interaction of a Schiff base derived from 2-hydroxyacetophenone and ethylenediamine (hapenH_2) with $M(CO)_6$, M = Cr and Mo, in THF under atmospheric pressure gave the oxo derivatives M(O)(hapen) with the metal atom in +4 formal oxidation state. IR spectra of the complexes revealed the presence of the M = O bond. The dihydride complex MoH_2(CO)(hapen) was also isolated from the reaction of $Mo(CO)_6$ and hapenH_2 under reduced pressure; ν(CO) and ν(Mo-H) frequencies were clearly indicated in its IR spectrum. The three complexes were found to be paramagnetic. Magnetic susceptibility measurements suggested that the d^4 Mo atom in MoH_2(CO)(hapen) exists in a low spin configuration. Electronic spectra of the ligand and its complexes in different donor solvents displayed bands due to compound-solvent, charge-transfer complexes.

Keywords: Schiff base; metal hydride; spectra; homogeneous catalysis; metal carbonyls

INTRODUCTION

Various metal carbonyl derivatives play an important role in homogeneous catalysis involving hydrogenation, hydroformylation, carbonylation and oxo transfer reactions [1]. Chromium, manganese, cobalt, nickel and ruthenium complexes with a wide variety of ligands having donor atom sets such as N_2O_2 and N_4 around the metal ion have been used as catalysts for epoxidation reactions [2]. These complexes bind reversibly to molecular oxygen with a change in oxidation state of the metal [3-6]. It was suggested that the oxygen atom is

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*Author for correspondence.

successively transferred from the terminal oxidant to the metal catalyst and then to the olefin [2]. The oxo(salen)chromium(V) complex was isolated from the catalytic reaction of Cr(III) salen and olefins in the presence of iodosylbenzene and its structure was determined by X-ray diffraction [3]. The oxochromium(V) adduct with pyridine-*N*-oxide as an axial ligand was also isolated and it epoxidized olefins. These results suggest that metal salen complexes catalyze epoxidation through the corresponding oxo species [3]. An active oxo species was also postulated in epoxidation using (salen)manganese(III) [4, 7] or (salen) nickel(II) [5] catalysts. Except for the oxochromium(salen) complexes, no other metal oxo species has been reported [2].

In this paper, we describe the reactions of the chromium and molybdenum hexacarbonyls with *bis*(2-hydroxyacetophenone)ethylenediimine, hapenH_2. Isolation and spectroscopic characterization of oxochromium and oxomolybdenum complexes as well as the molybdenum dihydride complex $MoH_2(CO)$(hapen) are reported.

EXPERIMENTAL

Reagents

The metal hexacarbonyls, $M(CO)_6$, M = Cr and Mo were supplied from Aldrich. All chemicals were of analytical reagent grade and they were used without further purification.

Synthesis of *bis*(2-hydroxyacetophenone)ethylenediimine, HapenH_2

The ligand hapenH_2 was synthesized by refluxing an ethanolic solution of 2-hydroxyacetophenone and ethylenediamine (2:1 molar ratio) for one hour. The reaction mixture was cooled and a bright yellow crystalline solid separated. The solid was filtered off and recrystallized from ethanol to give bright yellow crystals [8].

Synthesis of *bis*(2-hydroxyacetophenone)ethylenediimineoxochromium(IV)

A mixture of $Cr(CO)_6$ (0.05 g, 0.21 mmol) and hapenH_2 (0.06 g, 0.21 mmol) in about 30 cm^3 of THF was heated to reflux under atmospheric pressure for 2 days. The colour of the reaction mixture changed from yellow to reddish brown and a brown solid formed. The reaction mixture was then cooled and the dark brown precipitate separated by filtration and purified by refluxing it several times with THF followed by washing with hot petroleum ether. The complex was recrystallized from hot ethanol to give dark brown crystals, which were left to dry on a vacuum line for a few hours (yield, 52%); the complex was found to be moderately air stable.

Synthesis of *bis*(2-hydroxyacetophenone)ethylenediiminechromium(III) nitrate

Chromium(III) nitrate (0.10 g, 0.42 mmol) dissolved in the least amount of THF was added to a hot THF solution of hapenH_2 (0.10 gm, 0.37 mmol). Immediately, a greenish brown precipitate was obtained. The solid was filtered off, washed with THF several times and recrystallized from dimethylsulfoxide to give greenish brown crystals. The complex was dried on a vacuum line (yield, 83%).

Synthesis of *bis*(2-hydroxyacetophenone)ethylenediiminemonocarbonyl dihydridomolybdenum(II)

$Mo(CO)_6$ (0.10 g, 0.38 mmol) and hapenH_2 (0.11 g, 0.38 mmol) were mixed together in a sealed tube containing ~20 cm^3 of THF. The mixture was degassed with one freeze-thaw cycle and then heated for 20 h at 80°C. The colour of the solution changed to brown. The reaction mixture was cooled and the solvent removed on a vacuum line. The brown residue was washed several times with boiling petroleum ether. The complex was then recrystallized from THF to yield brown crystals, which were left to dry *in vacuo* for ~3 h (yield, 56%). The compound was found to be moderately air stable.

Synthesis of *bis*(2-hydroxyacetophenone)ethylenediimineoxomolybdenum (IV)

A mixture of $Mo(CO)_6$ (0.10 g, 0.38 mmol) and hapenH_2 (0.11 g, 0.38 mmol) in about 30 cm^3 of THF was heated to reflux under atmospheric pressure. The colour of the reaction mixture changed from yellow to orange after 30 minutes and then changed to brown and a dark brown solid separated after 48 h. The reaction mixture was cooled and the dark brown solid isolated by filtration. The isolated residue was purified by boiling it several times with THF followed by washing with hot petroleum ether. Recrystallization from hot ethanol gave dark brown crystals. The complex was left to dry on a vacuum line (yield, 65%); it was found to be moderately air stable.

Instrumentation

Infrared measurements were carried out on a Unicam-Mattson 1000 FT-IR spectrometer with the use of KBr discs. Electronic absorption spectra were measured with a Perkin-Elmer Lambda 4*β* spectrophotometer with 10.0 mm quartz cells. Samples of concentrations *ca* 1×10^{-6} M in dichloromethane, tetrahydrofuran, ethanol, dimethylformamide and dimethylsulfoxide were measured against the solvent in the reference cell. The nuclear magnetic resonance measurements were performed on a Spectrospin-Bruker AC 200 MHz NMR spectrometer. The samples were dissolved in DMSO-d_6 using tetramethylsilane as internal reference. The magnetic susceptibilities of the complexes in the solid state were recorded on a Sherwood Scientific magnetic susceptibility balance. Besides the spectroscopic studies, all complexes were characterized by elemental analysis and mass spectroscopy; data are given in Tables I-III.

RESULTS AND DISCUSSION

Reactions of the hexacarbonyls of chromium and molybdenum, $M(CO)_6$, with *bis*(2-hydroxyacetophenone)ethylenediimine in THF under atmospheric pressure resulted in the formation of the mononuclear complexes M(O)(hapen). On the other hand, when the reaction of $Mo(CO)_6$ with hapenH_2 was carried out under

TABLE I Elemental analysis and mass spectroscopic data for the chromium and molybdenum complexes.

Complex	*Elemental analysis* *% C*		*%H*		*% N*			*mass spectrometry*
	calc.	*found*	*calc.*	*found*	*calc.*	*found*	*Mol. Wt*	*m/z* (P^+)
Cr (O) (hapen)	59.6	59.3	5.0	5.1	7.7	7.9	362.35	363
Cr (hapen) NO_3	52.9	52.7	4.4	4.7	10.3	10.1	408.35	347 $(P\text{-}NO_3)^+$
MoH_2(CO)(hapen)	54.3	54.4	4.8	4.6	6.7	6.8	420.32	420 $(P\text{-}H)^+$
Mo(O)(hapen)	53.2	53.0	4.5	4.7	6.9	7.1	406.29	407

TABLE II Important IR data and magnetic moments for the chromium and molybdenum complexes.

Complex	*IR data* (cm^{-1})[a]		μ_{eff} *at 293 K (BM)*	
	$\nu_{(C\text{-}O)}$	$\nu_{(C=N)}$	$\nu_{(M\text{-}O)}$	
Cr(O) (hapen)	1245 (m)	1614 (s)	528 (w)[b]	2.25
Cr (hapen) NO_3	1237 (m)	1611 (s)	527 (w)[c]	3.52
MoH_2 (CO)(hapen)	1245 (m)	1615 (s)	477 (w)[d]	1.64
Mo(O) (hapen)	1241 (m)	1611 (s)	477 (w)[e]	1.42

[a] S, strong; m, medium; w, weak. [b] ν_{as} (Cr=O): 1306 (m) cm^{-1}; ν_s (Cr=O): 759 (m) cm^{-1}. [c] ν (NO_3^-): 1387 (s), 1010 (w) and 827 (w) cm^{-1}. [d] ν(CO): 1889 (s) cm^{-1}; ν (M-H): 1816 (m) cm^{-1}, δ(M-H): 677 (w) cm^{-1}. [e] ν_{as} (Mo=O): 944 (m) cm^{-1}; ν_s (Mo=O): 634 (w) cm^{-1}.

TABLE III Electronic spectroscopic data for hapenH_2 and its chromium and molybdenum complexes.

Compound			λ(nm)[a]		
	CH_2Cl_2	*THF*	*EtOH*	*DMF*	*DMSO*
hapenH_2	233 (24000)	251 (34600)	216 (23400)	266 (14600)	265 (27680)
	250 (sh) (17000)	320 (22000)	250 (11400)	319 (26000)	319 (26200)
	319 (b) (5600)		322 (b) (3200)	390 (b) (2400)	400 (sh) (2450)
			395 (b) (1700)		
Cr(O)(hapen)	235 (22000)	250 (26780)	216 (22510)	271 (21815)	266 (25680)
	276 (21280)	318 (10600)	250 (sh) (13070)	315 (16930)	316 (16070)
	340 (sh) (8430)	380 (sh) (3930)	320 (b) (5185)	380 (sh) (6985)	380 (sh) (6430)
			380 (sh) (2260)		
Cr(hapen) NO_3	235 (17950)	245 (9200)		270 (16840)	267 (27415)
	275 (sh) (6285)	274 (16415)	insol.	325 (13985)	
	385 (b) (1615)	390 (sh) (1970)			
MoH_2(CO) (hapen)	254 (22570)	250 (21430)		273 (23855)	272 (23615)
	288 (sh) (21000)	311 (20000)	insol.	314 (16000)	313 (14830)
	327 (b) (10340)				
Mo(O)(hapen)	234 (26485)	253 (21100)	216 (22315)	271 (19785)	265 (20740)
	250 (sh) (16230)	320 (9630)	250 (9815)	318 (20570)	316 (13985)
	318 (b) (6115)		325 (b) (3800)	400 (sh) (3500)	395 (sh) (3315)
			390 (b) (2230)		

[a] B, broad; sh, shoulder. Values of molar extinction coefficients, ϵ, are given in parentheses.

reduced pressure another complex, MoH_2(CO)(hapen), was isolated. The IR spectrum of the hapenH_2 ligand displayed bands due to ν(OH), ν(C=N) and ν(CO) at 3450, 1615 and 1245 cm^{-1}, respectively. The OH stretching frequency disappeared in the IR spectra of the complexes. On the other hand, the bands due to C=N and C-O moieties of the ligand were slightly shifted to lower frequencies in the corresponding IR spectra of the complexes (Table II). Furthermore, asymmetric and symmetric stretching frequencies due to M=O bonds were observed in the IR spectrum of both Cr(O)(hapen) and Mo(O)(hapen) complexes (Table II). The IR spectrum of MoH_2(CO)(hapen) complex also displayed a strong band in the metal carbonyl region at 1889 cm^{-1} due to the CO group. In addition, a weaker band at 2012 cm^{-1} in the spectrum could be assigned to ^{13}CO species in natural abundance. The ^{13}CO stretching vibration was assigned on the basis of its relative intensity and its separation from the strong ν(CO) band in accordance with the Teller-Redlich rule and the natural abundance of isotopes [9a]. The $\nu(^{13}CO)/\nu(^{12}CO)$ ratio for a number of transition metal carbonyl derivatives has a value of ~1 [9]; $\nu(^{13}CO)/\nu(^{12}CO)$ ratio for MoH_2(CO)(hapen) complex was found to be 1.06, which is in a good agreement with other reported values. The terminal M-H group exhibits a relatively sharp band of medium intensity in the 2250-1700 cm^{-1} region and its position is sensitive to other ligands on the metal. Also, it shows δ(M-H) in the 800-600 cm^{-1} region [10]. These bands exert shifts to lower frequencies by about 300-380 cm^{-1} on deuteration [10]. $MoH_2(CO)$(hapen) showed a sharp medium intensity band at 1816 cm^{-1} which could be assigned to ν(Mo-H) as well as a weak band at 677 cm^{-1} for δ(Mo-H). Attempts to synthesise the deuterated molybdenum complex were unsuccessful. However, no additional information could be abstracted from such an experiment because the expected ν(Mo-D) band might interfer with the other bands of the Schiff base in the range 1400-1550 cm^{-1}. The formulation of the molybdenum hydride complex was indicated from the elemental analysis as well as from mass spectrometry measurements. The latter method was previously used to detect the presence of the hydride ligand in metal carbonyl hydrides such as $H_4Ru_4(CO)_{12}$, $(C_5H_5)_2Zr(H)BH_4$ and $HMo_2(CO)_4(\mu\text{-}P(CH_3)_2)(C_5H_5)_2$ [11]. In the present investigation, we did not observe the molecular ion peak of the $MoH_2(CO)$(hapen) complex. Instead, the $(P\text{-}H)^+$ ion was detected at about 12% abundance. The presence of two hydride ligands was indicated from related ions such as $(P\text{-}CO)^+$, $(P\text{-}CH_3)^+$ and $(P\text{-}2CH_3)^+$, which were observed in fairly high abundances of 38.5, 18.6 and 82.0%, respectively.

Addition of a tetrahydrofuran solution of chromium(III) nitrate to a solution of $hapenH_2$ in THF led immediate formation of the complex [Cr(hapen)] NO_3 with the release of two equivalent hydrogen ions. The IR spectrum of the complex showed ν(C-O) and ν(C=N) frequencies similar to the other chromium and molybdenum complexes. Conductometric measurements of the complex in CH_2Cl_2 solutions gave conductances corresponding to a weak electrolyte (samples of concentrations 1×10^{-4} to 1×10^{-5} M gave conductance values from 1.7×10^{-6} to 0.5×10^{-6} ohm^{-1}). The presence of NO_3^- was also confirmed by IR spectroscopy (Table II) [10].

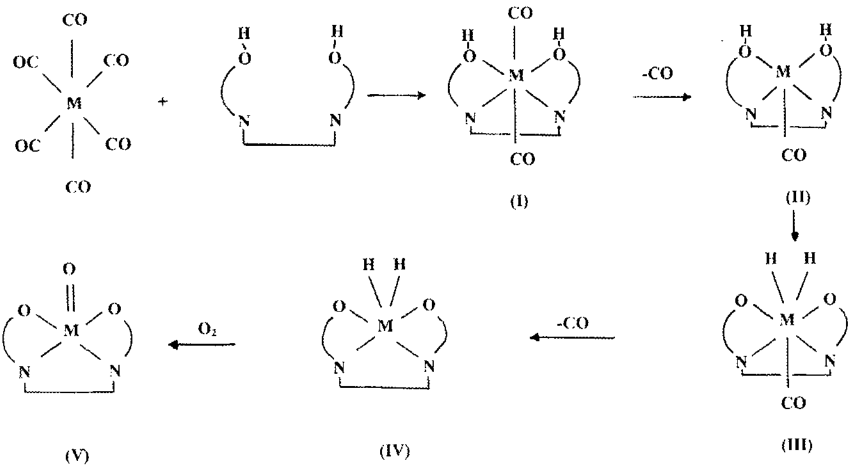
Investigation of the chromium and molybdenum complexes by ^1H NMR spectroscopy showed no signal for the hapen or hydride moieties. This behaviour is characteristic of paramagnetic materials. Therefore, the magnetic susceptibility of the solid complexes were measured at 293 K. For the chromium complexes Cr(O)(hapen), d^2, and $[Cr(hapen)]NO_3$, d^3, the effective magnetic moments (μ_{eff}) were found to be 2.25 and 3.52 BM, respectively. These values are less than the corresponding spin-only value (2.83 BM, for two unpaired electrons and 3.87 BM for three unpaired electrons). However, many previously reported chromium(III) complexes showed smaller effective magnetic moments than the spin-only moment. For example, $Cr(PhenSQ)_3$, PhenSQ = phenanthrenesemiquinone, $Cr(Cl_4SQ)_3$, Cl_4SQ = tetrachlorosemiquinone [12]. and $Cr(ChrySQ)_3$, ChrySQ = chrysenesemiquinone [13], exhibited μ_{eff} values of 1.15, 1.08 and 2.55 BM, respectively. Nevertheless, some chromium(III) complexes with Schiff bases derived from salicylaldehyde and amino acids showed magnetic moments of

~4.2 BM [14]. The two molybdenum complexes $MoH_2(CO)$(hapen), d^4, and Mo(O)(hapen), d^2, gave effective magnetic moment values of 1.64 and 1.42 BM, respectively. These two values are close and may indicate that the Mo(II) in $MoH_2(CO)$(hapen) has a low-spin electronic configuration [15]. However, these values could be due to second order paramagnetism effects arising from a low lying excited state in an otherwise diamagnetic compound; the diamagnetism might arise from further splitting of the t_{2g} orbitals in the low symmetry complexes. $Mo(CO)_6$ readily reacts with nitrogen, phosphorus and arsenic donor ligands with the replacement of one to four CO groups. Subsequent reaction of the resulting complexes with halogens afford a variety of six and seven coordinate Mo(I), Mo(II) and Mo(III) complexes. The magnetic properties of such species are complicated and magnetic moments were found in the range of 1.4-2.0 BM [15].

Chromium(III) Schiff base complexes were found to be readily converted to the corresponding oxochromium(V) species [3]. Oxygenation of some ruthenium(III) Schiff base derivatives also resulted in the reversible oxidation of Ru(III) to a formal Ru(IV) oxidation state with the reduction of O_2 to superoxide ion [6]. Reactions of these Ru(III) complexes with CO were also found to be reversible and the CO group can be displaced by flushing a stream of nitrogen through solutions of complexes [6]. On the other hand, investigation of various Co(II) complexes showed that the ligand environment and the ease with which the metal ion can be oxidized are important factors affecting the stability of dioxygen complexes [16-18].

We have found that $Mo(CO)_6$ reacts with hapenH_2 under reduced pressure to give $MoH_2(CO)$(hapen). Attempts to isolate the chromium analogue from the reaction of $Cr(CO)_6$ and hapenH_2 under reduced pressure were unsuccessful. On the other hand, the oxo complexes M(O)(hapen), M=Cr and Mo, were isolated from the corresponding reactions in air. It is interesting to speculate that $MoH_2(CO)$(hapen) was prepared through the intermediate II in Scheme 1. This five coordinate intermediate could be generated from the intermediate I by losing a CO molecule due to the *trans* labilization of CO [15]. Hydrogen transfer (oxidative addition) from the ligand to the metal atom in the intermediate II will result in the formation of the dihydride complex III with a change in the oxidation state of the metal from zero to +2. Complex III easily loses CO to give the intermediate IV (Scheme 1) [19]. The latter is easily oxidized to the oxo complex V [M(O)(hapen)] with a metal in +4 formal oxidation state.

The electronic absorption spectrum of hapenH_2 in CH_2Cl_2 displayed a band at 233 nm with a shoulder at 250 nm due to the benzenoid π-π^* transition. Also, the spectrum showed a band at 319 nm due to the n-π^* transition. By increasing the polarity of the solvent, the band at 233 nm disappeared and the shoulder was



pronounced and exhibited a bathochromic shift (Table III). The band at 319 nm did not show a significant shift although its intensity increased with increasing solvent polarity. In addition to the 250 and 322 nm bands, the spectrum of hapen H_2 in ethanol showed a strong UV band at 216 nm and a weak, broad band in the visible range at 395 nm, indicating the presence of two different species in equilibrium. The band at 250-266 nm could be assigned to a ligand-solvent charge-transfer complex of the n-π^* type (donation from the donor atom of the solvent to the phenyl ring of hapenH_2) [20]. In ethanol, 1:1 and 1:2 ligand to solvent charge transfer complexes might exist in equilibrium. The electronic absorption spectra of Cr(O)(hapen) and Mo(O)(hapen) in different solvents were similar (Table III), indicating that they have similar structures. On the other hand, MoH_2(CO)(hapen) gave two bands in the spectra and their positions depended upon the polarity of the solvent. However, all three complexes showed that the band of the ligand at 320 nm to undergo a hypsochromic shift except for MoH_2(CO)(hapen) in CH_2Cl_2 (Table III). Cr(O)(hapen) and Mo(O)(hapen) were the only complexes soluble in ethanol and they gave similar spectra to hapenH_2. Again, the highest energy UV band in the spectra was assigned to charge transfer between the complex and the solvent.

References

[1] J.P. Collman and L.S. Hegedus, *Principles and Applications of Organotransition Metal Chemistry*, (University Science Book, California, 1980).
[2] T. Katsuki, *Coord. Chem. Rev.*, **140**, 189 (1995).
[3] E.G. Samsel, K. Srinivasan and J.K. Kochi, *J. Am. Chem. Soc.*, **107**, 7606 (1985).
[4] K. Srinivasan, P. Michaud and J.K. Kochi, *J. Am. Chem. Soc.*, **108**, 2309 (1986).
[5] H. Yoon and C.J. Burrows, *J. Am. Chem. Soc.*, **110**, 4087 (1988).

[6] M.M. Taqui Khan, N.M. Khan, R.I. Kureshy and A.B. Boricha, *Inorg. Chim. Acta*, **174**, 175 (1990).
[7] C.P. Horwitz, S.E. Creager and R.W. Murray, *Inorg. Chem.*, **29**, 1006 (1990).
[8] (a) I.L. Finar, Organic Chemistry, 5th edn., (Longman, London, 1967); (b) H.Bahron, *Ph.D. Thesis*, (Univ. of Surrey, UK, 1994).
[9] (a) N.B. Colthup, L.H. Daly and S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, (Academic Press, New York, 1964); (b) E. Pitcher and F.G.A. Stone, *Spectrochim. Acta*, **18**, 585 (1962); (c) A.P. Hagen and A.G. MacDiarmid, *Inorg. Chem.*, **6**, 686 (1967); (d) R.K.Pomeroy, R.S.Gay, G.O.Evans and W.A.G.Graham, *J. Am. Chem. Soc.*, **94**, 272 (1972).
[10] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., (Wiley, New York, 1986).
[11] J. Lewis and B.F.G. Johnson, *Acc. Chem. Res.*, **1**, 245 (1968).
[12] R.M. Buchanan, S.L. Kessel, H.H. Downs, C.G. Pierpont and D.N. Hendrickson, *J. Am. Chem. Soc.*, **100**, 7894 (1978).
[13] R.M. Ramadan, W.H. Mahmoud, A.S. Attia and M.F. El-Shahat, *Spectrochim. Acta*, **49 A**, 117 (1993).
[14] D. Sattari, E. Alipour, S. Shirani and J. Amighian, *J. Inorg. Biochem.*, **45**, 115 (1992).
[15] F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th edn., (Wiley, New York, 1980).
[16] B.S. Tovrog, D.J. Kitko and R.S. Drago, *J. Am. Chem. Soc.*, **98**, 5144 (1976).
[17] D. Chen and A.E. Martell, *Inorg. Chem.*, **26**, 1026 (1987).
[18] R.J. Motekaitis and A.E. Martell, *Inorg. Chem.*, **27**, 2718 (1988).
[19] J.R. Norton, *Acc. Chem. Res.*, **12**, 139 (1979).
[20] R. Foster *Organic Charge Transfer Complexes*, (Academic Press, London, 1969).