

This article was downloaded by:

On: 23 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

### Interaction of SO<sub>2</sub> with unsaturated Schiff-base complexes; thermal, magnetic, and spectroscopic studies

Akila A. Saleh<sup>a</sup>; Abdel Razak M. Tawfik<sup>ab</sup>; Mosad A. El Ghamry<sup>a</sup>; Samy M. Abu-el-wafa<sup>a</sup>

<sup>a</sup> Faculty of Education, Department of Chemistry, Ain Shams University, Roxy, Cairo, Egypt <sup>b</sup> Department of Inorganic Chemistry, Ain Shams University, Cairo, Egypt

**To cite this Article** Saleh, Akila A. , Tawfik, Abdel Razak M. , El Ghamry, Mosad A. and Abu-el-wafa, Samy M.(2009) 'Interaction of SO<sub>2</sub> with unsaturated Schiff-base complexes; thermal, magnetic, and spectroscopic studies', *Journal of Coordination Chemistry*, 62: 20, 3377 – 3383

**To link to this Article:** DOI: 10.1080/00958970903060008

**URL:** <http://dx.doi.org/10.1080/00958970903060008>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Interaction of SO<sub>2</sub> with unsaturated Schiff-base complexes; thermal, magnetic, and spectroscopic studies

AKILA A. SALEH<sup>†</sup>, ABDEL RAZAK M. TAWFIK<sup>†‡</sup>,  
MOSAD A. EL GHAMRY<sup>†</sup> and SAMY M. ABU-EL-WAFA\*<sup>†</sup>

<sup>†</sup>Faculty of Education, Department of Chemistry, Ain Shams University,  
Roxy, Cairo, Egypt

<sup>‡</sup>Department of Inorganic Chemistry, Ain Shams University, Cairo, Egypt

(Received 6 March 2009; in final form 20 March 2009)

A series of Schiff-base complexes are prepared and characterized by elemental and thermal analyses, IR and electronic spectra, and magnetic measurements. SO<sub>2</sub> interacted with solutions of the complexes forming complexes [M(SB)(SO<sub>2</sub>)<sub>2</sub>] where M = Mg(II), Cu(II), Mn(II), and [M(SB)(SO<sub>2</sub>)<sub>2</sub>]OH where M = Fe(III). These complexes are subjected to elemental and thermal analyses, conductance measurements and IR, electronic, and ESR spectra to indicate changes from interaction of SO<sub>2</sub> with the Schiff-base complexes.

*Keywords:* Schiff-base complexes; SO<sub>2</sub> interaction; TGA; IR; UV-visible, ESR spectra

### 1. Introduction

Schiff-base complexes have attracted attention due to their structural diversity and potential applications in catalysis, sorption, electrical conductivity, magnetism, photochemistry, medicine, and material science [1–3]. Dianionic tetradentate Schiff-base complexes [4–16] have been examined, but little has been done on interactions with SO<sub>2</sub> [17, 18]. Here we describe a series of Schiff-base complexes. The complexes interact with SO<sub>2</sub> molecules to give a series of Schiff-base complexes with SO<sub>2</sub>.

### 2. Experimental

The chemicals used were from BDH. Solvents were purified by recommended procedures [19]. The apparatus, physical measurements, and analyses are as previously described [11, 17, 18].

#### 2.1. Physical measurements

Elemental microanalyses for C, H, and N were performed in the Microanalytical Center, Cairo University. Infrared spectra were recorded on a Perkin-Elmer FT-IR

\*Corresponding author. Email: smabuelwafa@hotmail.com

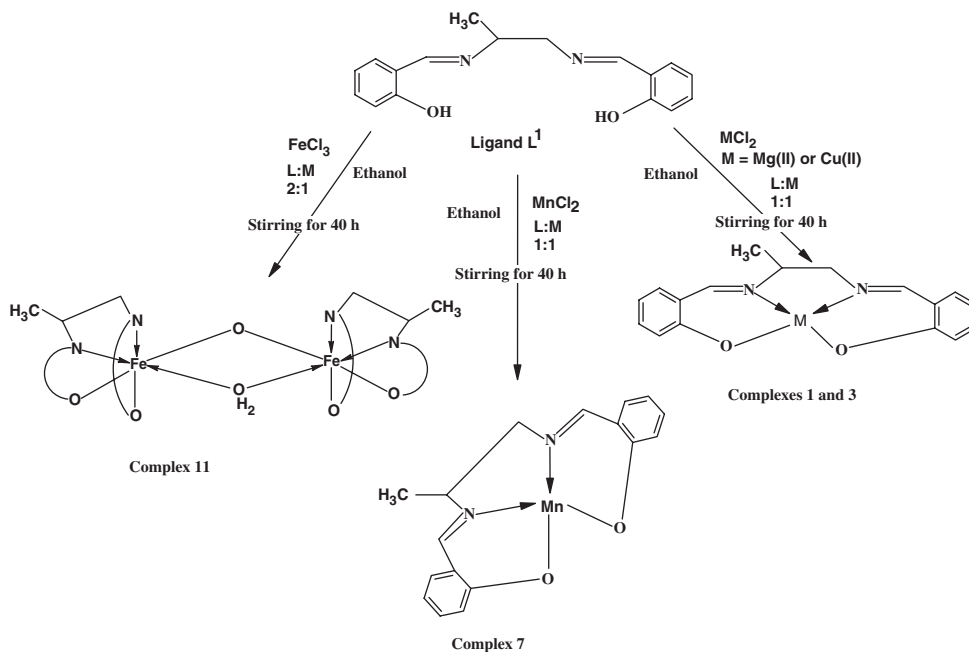
spectrometer using KBr discs. The UV-Vis spectra were recorded on a SHIMADZU UV-Vis spectrophotometer Model V-550 from 350 to 600 nm using Nujol mulls. Molar conductance of the complexes in DMF was measured using a Sybron-Barnstead conductometer. Magnetic moments of the complexes were determined at room temperature by the Gouy method on a (TM) Johnson Matthey Alpha Products Susceptibility Balance. Thermal analyses (TGA) were carried out in a dynamic nitrogen atmosphere ( $20 \text{ mL min}^{-1}$ ) with a heating rate of  $5^\circ\text{C min}^{-1}$  using a Shimadzu TGA-50H. The X-band ESR spectra of powder samples were recorded using a JES-FE2XG equipped with an E101 microwave bridge in the micro analytical center of Tanta University. The magnetic field was calibrated with 2,2-dipicryl hydrazyl. Metal contents were determined complexometrically using standard EDTA titration. The other physical measurements were carried out as previously described [20].

## 2.2. Preparation of Schiff-base complexes

The complexes  $[\text{MgL}^1]$ ,  $[\text{CuL}^1]$ ,  $[\text{CuL}^2]$ ,  $[\text{MnL}^1]$ ,  $[\text{MnL}^2]$ ,  $[(\text{FeL}^1)_2\text{OH}_2\text{O}]$ , and  $[(\text{FeL}^2)_2\text{OH}_2\text{O}]$  were prepared by literature method [20, 21] as illustrated in scheme 1 for  $\text{L}^1$  and Supplementary material for  $\text{L}^2$ .

## 2.3. Preparation of $[\text{ML}^1(\text{SO}_2)_2]$ or $[\text{ML}^2(\text{SO}_2)_2]$

$\text{ML}^1$  or  $\text{ML}^2$  (10 mmol) was dissolved in MeOH (50 mL) and a stream of  $\text{SO}_2$  was bubbled through the solution for 4 h. The solution was reduced in volume to 25 mL,



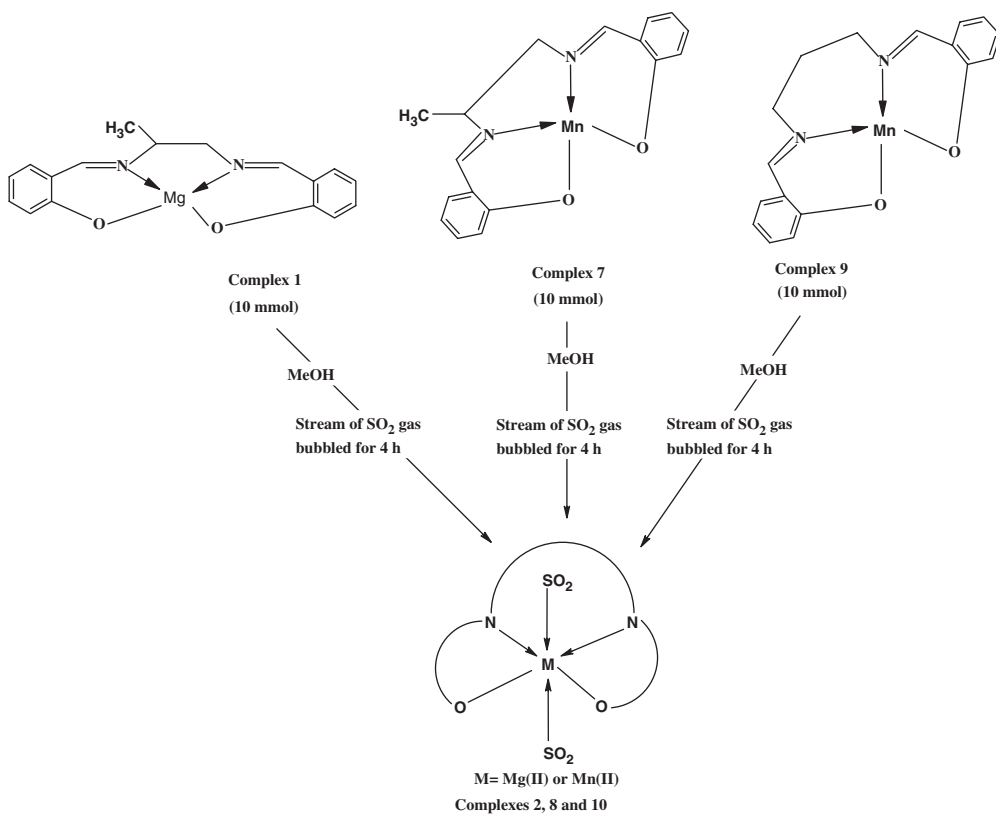
Scheme 1. Preparation of 1, 3, 7, and 11.

precipitated by diethyl ether and then dried *in vacuo* (scheme 2 and Supplementary material).

The complexes obtained were subjected to elemental analysis (table 1).  $\text{SO}_2$  in the complex was determined by dissolving 0.01 mol of the complex in 100 mL of aqueous  $\text{H}_2\text{O}_2$  (10 volume) and stirring the reaction mixture for 2 h till complete conversion of  $\text{SO}_2$  into  $\text{H}_2\text{SO}_4$ . The sulfate content was determined as  $\text{BaSO}_4$  [17].

### 3. Results and discussion

Analyses (table 1) indicate composition of [ML] (**1**, **3**, **5**, **7**, and **9**),  $[(\text{ML})_2(\text{O})(\text{H}_2\text{O})]$  (**11** and **13**), and  $[\text{ML}(\text{SO}_2)_2]$  (**2**, **4**, **6**, **8**, **10**, **12**, and **14**) complexes. The Schiff bases are dibasic tetradentate toward the metal ions, also supported from the conductance values ( $7.0\text{--}13.0\ \text{Ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ ) within the range for nonelectrolytes [22]. Interaction of  $\text{SO}_2$  leads to the coordination of  $2\text{SO}_2$  molecules to M(II).



Scheme 2. Preparation of **2**, **8**, and **10**.

Table 1. Microanalysis results and ESR  $g_{\text{eff}}$ -values of some Schiff-base complexes.

Complex No.	Complex	m.p. (°C).	Color	Microanalysis data						ESR $g_{\text{eff}}$ -values				
				C <sup>a</sup>	H <sup>a</sup>	N <sup>a</sup>	S <sup>a</sup>	M <sup>a</sup>	$\Lambda^b$	$\mu_{\text{eff}}^c$	$g_x = g_{11}$	$g_y$	$g_z = g_1$	$g_{\text{eff}}$
1	MgL <sup>1</sup>	260	Lemon yellow	66.82 (67.03)	5.02 (5.25)	9.46 (9.20)	—	7.76 (7.98)	—	—	—	—	—	—
2	[MgL <sup>1</sup> (SO <sub>2</sub> ) <sub>2</sub> ]	240	White	47.32 (47.18)	3.88 (3.70)	6.25 (6.47)	14.65 (14.80)	5.53 (5.62)	8.6	—	—	—	—	—
3	CuL <sup>1</sup>	232	Deep violet	59.64 (59.38)	4.33 (4.65)	7.95 (8.15)	—	18.70 (18.49)	—	2.1	—	—	—	1.7795
4	[CuL <sup>1</sup> (SO <sub>2</sub> ) <sub>2</sub> ]	228	Light brown	43.33 (43.26)	3.53 (3.39)	6.02 (5.93)	13.77 (13.57)	13.62 (13.47)	10.5	1.9	2.2772	2.0449	1.8156	2.0546
5	CuL <sup>2</sup>	250	Deep green	59.53 (59.38)	4.80 (4.65)	8.02 (8.15)	—	18.60 (18.49)	—	1.7	—	—	—	1.7007
6	[CuL <sup>2</sup> (SO <sub>2</sub> ) <sub>2</sub> ]	205	Deep brown	43.45 (43.26)	3.12 (3.39)	5.78 (5.93)	13.38 (13.57)	13.25 (13.47)	11.2	1.5	2.0512	2.1057	2.1449	2.2047
7	MnL <sup>1</sup>	190	Dark brown	60.70 (60.90)	4.63 (4.77)	8.15 (8.35)	—	16.75 (16.40)	—	5.6	—	—	—	—
8	[MnL <sup>1</sup> (SO <sub>2</sub> ) <sub>2</sub> ]	105	Gray	43.92 (44.06)	3.23 (3.45)	5.88 (6.04)	13.76 (13.82)	12.09 (11.86)	7.0	5.4	—	—	—	—
9	MnL <sup>2</sup>	250	Dark brown	60.85 (60.90)	4.56 (4.77)	8.25 (8.35)	—	16.02 (16.40)	—	5.8	—	—	—	1.9385
10	[MnL <sup>2</sup> (SO <sub>2</sub> ) <sub>2</sub> ]	192	Light brown	43.88 (44.06)	3.61 (3.45)	5.98 (6.04)	13.65 (13.82)	11.97 (11.86)	7.4	5.3	—	—	—	1.9587
11	[(FeL <sup>1</sup> ) <sub>2</sub> OH <sub>2</sub> O]	250	Red brown	57.57 (57.81)	4.81 (4.53)	8.05 (7.93)	—	16.21 (15.82)	—	5.7	—	—	—	—
12	[FeL <sup>1</sup> (SO <sub>2</sub> ) <sub>2</sub> ]OH	215	Light brown	44.02 (42.43)	3.58 (3.54)	5.96 (5.82)	13.68 (13.31)	11.89 (11.61)	8.0	4.0	—	—	—	—
13	[(FeL <sup>2</sup> ) <sub>2</sub> OH <sub>2</sub> O]	280	Red brown	57.52 (57.81)	4.85 (4.53)	8.25 (7.93)	—	16.35 (15.82)	—	5.9	—	—	—	—
14	[FeL <sup>2</sup> (SO <sub>2</sub> ) <sub>2</sub> ]OH	235	Deep violet	43.87 (42.43)	3.25 (3.54)	5.93 (5.82)	13.72 (13.31)	11.88 (11.61)	13.0	4.1	—	—	—	—

Notes: <sup>a</sup>% Found (% Calcd).<sup>b</sup>Ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, 10<sup>-3</sup> M in DMF solution.<sup>c</sup>B.M.

### 3.1. TGA studies

Thermograms (Supplementary material) of  $[\text{CuL}^1]$  and  $[\text{CuL}^2]$  (**3** and **5**) have one decomposition step, thermally stable to 300 and 320°C, respectively, followed by the formation of CuO. Thermograms of  $[\text{CuL}^1(\text{SO}_2)_2]$  and  $[\text{CuL}^2(\text{SO}_2)_2]$  complexes (**4** and **6**) have three and five decomposition steps, completely different from  $[\text{CuL}^1]$  and  $[\text{CuL}^2]$ .  $\text{SO}_2$  containing complexes decompose in two overlapping steps starting at 200–260°C for **4**. Complex **6** loses  $\text{SO}_2$  in two steps at 120 and 160°C, respectively. The ligands in **4** and **6** start decomposing at 265–310°C for **4** and 165–420°C for **6**. Weight loss of  $\text{SO}_2$  molecules during the first and second steps for **4** and **6**, found (Calcd), are 27.45(27.14) and 27.46(27.14), respectively. TGA indicates that  $\text{SO}_2$  is bounded to Cu(II).

### 3.2. IR spectra

IR spectra of **1**, **3**, **5**, **7**, **9**, **11**, and **13** indicate two  $\nu_{\text{C}=\text{N}}$  absorption bands situated at 1635–1627 and 1638–1630  $\text{cm}^{-1}$ , respectively, and  $\nu_{\text{M}-\text{O}}$  and  $\nu_{\text{M}-\text{N}}$  at 450–472 and 359–399  $\text{cm}^{-1}$ , respectively, consistent with dianionic tetradentate Schiff-base coordination [21]. Interaction of  $\text{SO}_2$  (**2**, **4**, **6**, **8**, **10**, **12**, and **14**) leads to obvious changes in the IR spectra of the complexes:  $\nu_{\text{C}=\text{N}}$  at 1610–1625  $\text{cm}^{-1}$  indicates that the interaction of  $\text{SO}_2$  causes shift to lower frequency by 10–17  $\text{cm}^{-1}$ . Bands at 1106–1147, 917–930, and 416–425  $\text{cm}^{-1}$ , absent in the spectra of parent complexes, can be assigned to  $\nu_3$ ,  $\nu_1$ , and  $\nu_2$  of  $\text{SO}_2$  [23, 24]. Positions of  $\nu_3$ ,  $\nu_1$ , and  $\nu_2$  indicate coordination to M(II) through sulfur in **2**, **4**, **6**, **8**, and **10**. For **12** and **14**, positions of  $\nu_3$ ,  $\nu_1$ , and  $\nu_2$  lead us to conclude that  $\text{SO}_2$  coordinates bridging bidentate through S and O [18, 25, 26]. Far infrared indicates that M–O and M–N absorption bands occur at 488–456 and 396–369  $\text{cm}^{-1}$ , respectively. For Fe(III) complexes **11** and **13**,  $\nu_{\text{OH}}$  bands at 3400 and 3440 indicate OH of water [18, 27, 28].

### 3.3. UV-visible spectra

Visible reflectance spectra of the complexes under investigation indicate the following results. Complexes **1** and **2** show absorption bands situated at 367–396 and 416–424 nm assigned as C=N and CT, respectively. For **3** and **5**, the spectra show four absorption bands, 327–363, 424–429, 546–616, and 593–686 nm; the first two bands can be assigned to C=N and CT transitions while the third and the fourth can be assigned to transitions corresponding to  ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$  and  ${}^2\text{E}_{1g} \rightarrow {}^2\text{T}_{2g}$ , respectively, indicating square planar geometry around Cu(II) [29]. For **4** and **6** (when  $\text{SO}_2$  molecules are coordinated), the spectra show four absorption bands at 366–394, 429–442, 649–701, and 787–806 nm; the first two bands are assigned to  $\pi \rightarrow \pi^*$  of the C=N and CT transitions while the third and fourth band can be assigned to  ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$  and  ${}^2\text{E}_{1g} \rightarrow {}^2\text{T}_{2g}$ , confirming octahedral geometry around Cu(II) [20]. Complexes **7** and **9** show three absorption bands at 378–419, 401–461, and 470–473 nm; the first band can be assigned to C=N while the second and third are assigned to  ${}^6\text{T}_1 \rightarrow {}^4\text{T}_2(\text{G})$  and  ${}^2\text{T}_1 \rightarrow {}^4\text{T}_1$  for tetrahedral Mn(II) [30, 31]. In **8** and **10** (when  $\text{SO}_2$  molecules are coordinated), the spectra show bands at 411–421, 570–650, and 652–775 nm, the first band assigned to  $\pi \rightarrow \pi^*$  of C=N and the second and third bands to  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$  and  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$ , respectively, for octahedral Mn(II). Complexes **11** and **13** show four absorption bands at 394–427, 424–471, 604–623, and 667–668 nm; the first two are assigned to  $\pi \rightarrow \pi^*$  of the C=N

and CT and the third and fourth to  ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$  and  ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$  for octahedral Fe(III). Interaction of  $SO_2$  (**12** and **14**) have four absorption bands at 402–470, 424–509, 535–554, and 779–792 nm, respectively, the first two assigned to  $\pi \rightarrow \pi^*$  of C=N and CT and the third and fourth to  ${}^6A_{1g} \rightarrow {}^1T_{1g}$  and  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  for octahedral Fe(III).

### 3.4. Magnetic studies

Magnetic moments of Cu(II) and Mn(II) complexes (**3**, **5**, **7**, and **9**) lie within the expected range 1.7–2.1 and 5.6–5.8 B.M., respectively (table 1). Fe(III) mono oxo-bridged complexes (**11** and **13**) have very different magnetic behavior with magnetic moments approaching zero at low temperature, but tending toward 5.7 and 5.9 B.M., respectively, at room temperature. The magnetic susceptibility measurements for **4**, **6**, **8**, **10**, **12**, and **14** were  $\mu_{\text{eff}} = 1.5\text{--}1.9$  ( $d^9$ ),  $5.3\text{--}5.4$  ( $d^5$ ) B.M./metal ion, lower than the expected values. Perhaps the Schiff base with more bulky substituents favor formation of polymeric species in the solid state [18, 29, 31].

### 3.5. ESR spectral studies

X-Band ESR spectra of powders of **3**, **4**, **5**, **6**, **9**, and **10** at room temperature are shown in Supplementary material and  $g$ -values are listed in table 1. Comparing ESR spectra of the Schiff-base complexes with those having  $SO_2$  coordinated show the following results.

In **3** and **5** only one anisotropic signal is observed whereas in **4** and **6** the number of signals increases with three anisotropic signals observed. The pattern,  $g_{\text{eff}}$  values and shape of the signals are completely different in complexes having  $SO_2$ . Complexes **4** and **6** reflect octahedral geometry around Cu(II). For **9** and **10**, the number and shape of signals depend on  $SO_2$  coordination. In **10** a number of signals overlap with an obvious change in the  $g_{\text{eff}}$  values; the pattern and shape of the signals reflect octahedral geometry around Mn(II) coordinated with  $SO_2$  [17, 32].

## 4. Conclusion

Interaction of  $SO_2$  with Schiff-base metal ion complexes leads to change in decomposition, color, and structure of the complexes (**1**, **3**, **5**, square planar) and (**7**, **9**, tetrahedral) to (**2**, **4**, **6**, **8**, and **10**, octahedral). In the case of Fe(III) complexes the  $SO_2$  molecules coordinated to Fe(III) cleaving the dimers to **12** and **14**.

## References

- [1] D.L. Long, E. Burkholder, L. Cronin. *Chem. Soc. Rev.*, **36**, 105 (2007).
- [2] S. Kuwata, M. Hidai. *Coord. Chem. Rev.*, **213**, 211 (2001).
- [3] K.E. Percy, A.H. Legge, S.V. Krupa. *Dev. Environ. Sci.*, **3**, 85 (2003).
- [4] J.P. Holland, P.J. Barnard, S.R. Bayly, J.R. Dilworth, J. Green. *Inorg. Chim. Acta*, **362**, 402 (2009).

- [5] T.M. Salama, I.O. Ali, A.I. Hanafy, W.M. Al-Meligy. *Mater. Chem. Phys.*, **113**, 159 (2009).
- [6] A. Stamatidis, P. Doutsis, C. Vartzouma, K.C. Christoforidis, Y. Deligiannakis, M. Louloudi. *J. Mol. Catal. A: Chem.*, **297**, 44 (2009).
- [7] V.K. Jain, L. Jain. *Coord. Chem. Rev.*, **249**, 3075 (2005).
- [8] M.L.N. Rao, H. Hoyou, K. Hiratoni. *Chem. Commun.*, 420 (2002).
- [9] J.-L. Liang, X.-Q. Yu, C.-M. Che. *Chem. Commun.*, 124 (2002).
- [10] S.M. Abu-El-Wafa, K.Y. El-Baradie, R.M. Issa. *Egypt J. Chem.*, **45**, 743 (2002).
- [11] Z. Liu, F.C. Anson. *Inorg. Chem.*, **40**, 1329 (2001).
- [12] A.M. Ramadan, W. Sawodny, R.M. Issa, H.Y.F. El-Baradi. *Egypt. J. Chem.*, **43**, 285 (2000).
- [13] N.J. Henson, P.J. Hay, A. Redondo. *Inorg. Chem.*, **38**, 1618 (1999).
- [14] J.M. McInnes, D. Swallow, A.J. Blake, P. Mountford. *Inorg. Chem.*, **37**, 5970 (1998).
- [15] A. Böttcher, T. Takeuchi, K.I. Hardcastle, T.J. Meade, H.B. Gray. *Inorg. Chem.*, **36**, 12 (1997).
- [16] C.A. McAuliffe, R.V. Parish, S.M. Abu El-Wafa, R.M. Issa. *Inorg. Chim. Acta*, **115**, 91 (1986).
- [17] S.M. Abu-El-Wafa, R.M. Issa. *Bull. Soc. Chem. France*, **88**, 37 (1989).
- [18] (a) F. Register. *Department of Labor: Occupation Exposure to Sulphur Dioxide*, **40**, 54520 (1975);  
(b) Cincinnati, *A.C.G.I.H: Sulphur Dioxide, Documentation of the TLVs for Substances in Work Room, Air. Ed. 3*, 238 (1974).
- [19] A.A. Saleh, S.M.E. Khalil, M.F. Eid, M.A. El ghamry. *J. Coord. Chem.*, **56**, 476 (2003).
- [20] K.A.R. Salib, A.A. Saleh, S.M. Abu El-Wafa, H.F.O. El Shafiy. *J. Coord. Chem.*, **56**, 283 (2003).
- [21] M.J. MacLachlan, M.K. Park, L.K. Thompson. *Inorg. Chem.*, **35**, 5492 (1996).
- [22] W.L. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).
- [23] J.R. Dilworth, C.A. McAuliffe, B.J. Sayle. *J. Chem. Soc., Dalton Trans.*, 849 (1977).
- [24] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edn, Wiley Interscience, New York (1986).
- [25] L.B. Booth, C.A. McAuliffe, C.L. Stanley. *J. Inorg. Met. Chem.*, **226**, 191 (1982).
- [26] F.A. Cotton, G. Wilkinson. *Advanced Inorganic Chemistry*, 3rd Edn, Wiley Interscience, New York (1972).
- [27] G.J. Kubas, R.R. Ryan, V. McCarty. *Inorg. Chem.*, **19**, 3003 (1980).
- [28] M.A. El-Ries, S.M. Abu-El-Wafa, F.A. Aly, M.A. El-Behairy. *Anal. Lett.*, **18**, 1905 (1985).
- [29] S.M. Abu-El-Wafa, M. Gaber, R.M. Issa, T.M. Ismail. *Bull. Soc. Chem. France*, **1**, 31 (1983).
- [30] F.A. Cotton, D.M.I. Gave, A. Sacce. *J. Am. Chem. Soc.*, **83**, 4175 (1961).
- [31] W.C. Polter, L.T. Taylor. *Inorg. Chem.*, **15**, 1329 (1976).
- [32] R.D. Wilson, J.A. Ibers. *Inorg. Chem.*, **17**, 2134 (1978).