

Contents lists available at SciVerse ScienceDirect

# Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



journal homepage: www.elsevier.com/locate/saa

# Spectroscopic studies on some fluorescent mixed-ligand titanium(IV) complexes

# Balram Prasad Baranwal\*, Alok Kumar Singh, Anand Varma

Coordination Chemistry Research Laboratory, Department of Chemistry, DDU Gorakhpur University, Gorakhpur 273009, India

#### ARTICLE INFO

Article history: Received 30 June 2011 Received in revised form 8 September 2011 Accepted 9 September 2011

Keywords: Titanium(IV) Fluorescent Mononuclear Mixed-ligand complexes

## ABSTRACT

A novel route to synthesize some titanium(IV) complexes containing acetylacetone, straight chain carboxylic acid and hydroxycarboxylic acid ligands has been investigated. Complexes with the general formula  $[Ti(acac)Cl_{2-n}(OOCR^*)_n(OOCC_{15}H_{31})]$  (where Hacac = acetylacetone, R\*COOH = hydroxycarboxylic acids and n = 1 or 2) have been isolated and characterized. Molecular weight determinations indicated mononuclear nature of the complexes. LMCT bands were observed in the electronic spectra. Infrared spectra suggested bidentate nature of the ligands. Fluorescent behaviour of the complexes was noticed on the basis of fluorescence spectra. Powder XRD indicated them to be semi-crystalline having the crystallite size in 136–185 nm range. Transmission electron microscopy (TEM) indicated spherical particles of ~200 nm diameter. On the basis of physico-chemical studies, it is suggested that titanium is having coordination number 7 or 8 in these complexes.

© 2011 Elsevier B.V. All rights reserved.

#### 1. Introduction

Although the chemistry of hydroxy (OH) rich ligands with oxometal centres such as VO<sup>2+</sup>, VO<sup>3+</sup>, cis-VO<sub>2</sub><sup>+</sup>, cis-MoO<sub>2</sub><sup>2+</sup> and trans-UO<sub>2</sub><sup>2+</sup>, is well understood [1], their coordination behaviour towards non-oxo metal species has received a limited attention [2]. The coordination role of hydroxy rich ligands with non-oxo metal centres, particularly in case of titanium(IV) is reported showing reactivity of cis-bis(acetylacetonate) and other  $bis(\beta$ -diketonate) complexes for many applications [3,4]. A perusal of the literature reveals that a number of transition metals form complexes with hydroxycarboxylic ligands [5], but studies on titanium(IV) complexes with such ligands are very limited. It has also been found that the mixed-ligand complexes of titanium(IV) with higher fatty acids and hydroxycarboxylic acids are not reported so far. Research on the synthesis and applications of fluorescent titanium(IV) complexes are currently considered as one of the most expanding areas in biomedical and inorganic chemistry [6].

Most of the titanium complexes are sensitive to hydrolysis which may cause a subsequent reduction in their catalytic property [7]. Their rate of hydrolysis can significantly be reduced resulting in better photocatalytic activity by using bulky electron-rich ligands [8]. In this light we have recently reported some titanium(IV) complexes having Ti–O–C bond and increased resistance towards hydrolysis [9].

In this paper we report an easier method of synthesis for nanosized, fluorescent mixed-ligand complexes of titanium(IV) in which

E-mail address: drbpbaranwal@gmail.com (B.P. Baranwal).

titanium is attached with all the different type of four ligands. The ligands chosen in this work were electron rich bearing hydroxy (OH) group keeping in view to result in a hydrolysis resistant products. Carboxylic and hydroxycarboxylic acids have been used in the light that incorporation of these ligands in titanium(IV) complexes may enhance the cytotoxicity providing a better candidate for anticancer agents [10]. These complexes are characterized using different spectral techniques and their coordination behaviour is discussed.

# 2. Experimental

#### 2.1. Materials and analytical methods

All the reactions were carried out under anhydrous conditions. Organic solvents (Qualigens) were dried and distilled before use by standard methods [11]. Sodium palmitate, acetylacetone, hydroxycarboxylic (salicylic, mandelic and benzilic) acids (Aldrich) and TiCl<sub>4</sub> (BDH) were used as received. Titanium and chlorine were estimated gravimetrically as TiO<sub>2</sub> and AgCl, respectively [12].

#### 2.2. Physico-chemical measurements

Electronic spectra were recorded on Hitachi U-2000 spectrophotometer in toluene. Fluorescence spectra were recorded on a Hitachi F-2500 spectrophotometer with the scan speed of 300 nm/min and PMT voltage at 400 V in toluene. Excitation source was 150 W Xenon lamp. Infrared spectra were recorded on a Perkin-Elmer RX1 FTIR spectrophotometer using KBr discs. <sup>1</sup>H NMR spectra were recorded at 300 MHz on a Bruker DRX-300 NMR spectrometer in CDCl<sub>3</sub>. Molecular weights were determined in a semi-micro

<sup>\*</sup> Corresponding author. Tel.: +91 551 2203459.

<sup>1386-1425/\$ -</sup> see front matter © 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2011.09.017

ebulliometer (Gallenkamp) with a thermistor sensing device. Powder XRD data were collected on a PW 1710 diffractometer. The operating voltage of the instrument was 30 kV and the operating current was 20 mA. The intensity data were collected at room temperature over a  $2\theta$  range of  $5.025-79.925^{\circ}$  with a continuous scan mode. Transmission electron microscopy (TEM) images were obtained on a Tecnai 30 G<sup>2</sup>S – Twin electron microscope with an accelerating voltage of 300 kV on the surface of a carbon coated copper grid. Molar conductance were measured on century CC-601 digital conductivity meter at  $10^{-2}$  to  $10^{-3}$  molar solutions in nitrobenzene. Solid state conductance measurements were carried out with Keithley 6220 Precision current source and keithley 2182 A nanovoltmeter. Elemental analyses (C, H) were done on a Vario EL III Carlo Erba 1108 elemental analyzer.

## 2.3. Synthesis of $[Ti(acac)Cl(OOCC_6H_4OH)(OOCC_{15}H_{31})]$ (1)

Synthesis of this complex was completed in following steps:

#### 2.3.1. Preparation of sodium salicylate

A solution of sodium metal (0.45 g, 19.57 mmol) in 25 mL of isopropanol (sodium isopropoxide formed in situ) was slowly added to chloride formed during the reaction was filtered out. Excess solvent from the soluble part was removed *in vacuo* to yield an orange solid. It was purified in dichloromethane-n-hexane mixture (1:1 ratio).

#### 2.4. Synthesis of [Ti(acac)(OOCC<sub>6</sub>H<sub>4</sub>OH)<sub>2</sub>(OOCC<sub>15</sub>H<sub>31</sub>)] (**2**)

Sodium salt of salicylic acid (1.04 g, 6.50 mmol) was added in the solution of **B** (1.54 g, 3.25 mmol) in benzene (50 mL). The contents were stirred (10 h) followed by refluxing (6 h). Insoluble sodium chloride formed during the reaction was filtered out. Excess solvent from the soluble part was removed *in vacuo* to yield dark orange solid. It was purified by using a mixture of dichloromethane and n-hexane (1:1 ratio).

An analogous procedure was adopted to synthesize other titanium(IV) complexes being reported in this communication and the details of analytical results are summarized in Table 1.

#### 3. Results and discussion

Some mixed-ligand complexes of titanium(IV) were synthesized by stepwise substitutions of chloride ions from titanium tetrachloride as depicted below:



Ρ"ΧΟΟΝα

Ρ'ΧΟΟΝα

Ρ'''ΧΟΟΝα

salicylic acid (2.70 g, 19.55 mmol) in isopropanol (25 mL). The contents were boiled to reflux for 3 h. Removal of excess isopropanol under vacuum yielded solid sodium salicylate (yield: calcd. = 3.13 g; found = 2.68 g).

#### 2.3.2. Preparation of $[Ti(acac)Cl_3](\mathbf{A})$

Acetylacetone (1.66 g, 16.68 mmol) was added to titanium tetrachloride (3.51 g, 16.61 mmol) taken in benzene (40 mL). Hydrogen chloride gas was evolved and the reaction was exothermic with a sharp colour change from yellow to red. The contents were refluxed for 4 h. Excess solvent was removed *in vacuo* and a dark red solid product **A** was obtained (yield: calcd. = 4.21 g; found = 3.49 g) [13].

#### 2.3.3. Preparation of [Ti(acac)Cl<sub>2</sub>(OOCC<sub>15</sub>H<sub>31</sub>)] (**B**)

Sodium palmitate (2.54 g, 9.12 mmol) was added to **A** (2.31 g, 9.12 mmol) taken in benzene (40 mL). The reaction mixture was stirred for 8 h followed by refluxing for 2 h. The contents were filtered using G 4 sieve to remove insoluble sodium chloride formed during the reaction. Excess solvent was removed *in vacuo* and a yellow coloured solid, **B** was obtained (yield: calcd.=4.32 g; found = 3.72 g) [9].

To a solution of  $\mathbf{B}(1.70 \text{ g}, 3.59 \text{ mmol})$  in benzene (50 mL), sodium salt of salicylic acid (0.58 g, 3.62 mmol) was added. The contents were stirred for 10 h followed by refluxing for 4 h. Insoluble sodium

where Hacac = acetylacetone;  $R^* = C_6H_4OH$  (R');  $C_6H_5CH(OH)$  (R") or  $(C_6H_5)_2C(OH)$  (R") and n = 1 or 2.

Benzene was chosen a solvent in these substitutions because sodium chloride formed during the reaction was insoluble and the titanium(IV) complexes were soluble which could made the separation easy. The molar conductance of complexes at  $10^{-2}$  to  $10^{-3}$ molar concentrations in nitrobenzene was obtained in the range  $3-9 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  which indicated them to be non-electrolytes [14]. Solid state conductance measurements were done for all the complexes and were found in the range  $1.4 \times 10^6 \text{--} 2.5 \times 10^6 \, \Omega$  at 295 K using current  $1 \times 10^{-8}$  A and voltage  $1.4 \times 10^{-2}$  V. This clearly indicated them to show high resistance or they could be said to behave like insulators. Room temperature magnetic moment measurements indicated diamagnetic nature of the complexes, showing absence of unpaired electrons in these complexes. They are characterized by elemental analyses too. Ebullioscopic method of molecular weight determinations showed that all the complexes were monomeric in refluxing benzene (Table 1).

#### 3.1. Electronic and fluorescence spectra

Two bands were observed in the range 202–208 nm and 288–305 nm in the electronic spectra of the complexes which could be assigned to  $\pi - \pi^*$  and  $n - \pi^*$  transitions, respectively. The electronic transitions observed in the range 362–445 nm are due to

# Table 1

Analytical results for titanium(IV) complexes.

Reactants (g, mmol)	Product (colour) (% yield)	MP (°C)	Found (calculated) %			Molecular weight found (calcd.)	
			Ti	Cl	С	Н	
[Ti(acac)Cl <sub>2</sub> (OOCC <sub>15</sub> H <sub>31</sub> )] + R'COONa	TiC <sub>28</sub> H <sub>43</sub> O <sub>7</sub> Cl	215	8.28	6.26	58.41	7.33	587
(1.70, 3.59) (0.58, 3.62)	(Orange) (86) (1)		(8.33)	(6.17)	(58.49)	(7.55)	(574)
[Ti(acac)Cl <sub>2</sub> (OOCC <sub>15</sub> H <sub>31</sub> )] + R'COONa	TiC <sub>35</sub> H <sub>48</sub> O <sub>10</sub>	224	7.21		62.28	7.10	668
(1.54, 3.25) (1.04, 6.50)	(Dark orange) (89) ( <b>2</b> )		(7.08)	-	(62.12)	(7.17)	(676)
[Ti(acac)Cl <sub>2</sub> (OOCC <sub>15</sub> H <sub>31</sub> )] + R"COONa	TiC <sub>29</sub> H <sub>45</sub> O <sub>7</sub> Cl	172	8.19	5.95	59.05	7.57	595
(1.84, 3.89) (0.68, 3.91)	(Dark yellow) (81) ( <b>3</b> )		(8.13)	(6.02)	(59.13)	(7.72)	(589)
[Ti(acac)Cl <sub>2</sub> (OOCC <sub>15</sub> H <sub>31</sub> )]+R"COONa	TiC <sub>37</sub> H <sub>52</sub> O <sub>10</sub>	184	6.63		63.01	7.29	715
(1.61, 3.40) (1.19, 6.83)	(Dark yellow) (78) ( <b>4</b> )		(6.79)		(63.06)	(7.45)	(704)
[Ti(acac)Cl <sub>2</sub> (OOCC <sub>15</sub> H <sub>31</sub> )]+R <sup>'''</sup> COONa	TiC <sub>35</sub> H <sub>49</sub> O <sub>7</sub> Cl	198	7.08	5.18	63.32	7.33	677
(1.16, 2.45) (0.62, 2.48)	(Yellow) (88) (5)		(7.20)	(5.33)	(63.20)	(7.44)	(665)
[Ti(acac)Cl <sub>2</sub> (OOCC <sub>15</sub> H <sub>31</sub> )]+R <sup>m</sup> COONa	TiC <sub>49</sub> H <sub>60</sub> O <sub>10</sub>	210	5.45		68.81	7.01	848
(1.53, 3.23) (1.62, 6.47)	(Yellow) (84) ( <b>6</b> )		(5.59)	-	(68.68)	(7.07)	(856)

#### Table 2

Fluorescence spectral data for titanium(IV) complexes.

Complex	Excitation $\lambda_{max}$	Apex (nm)	Region	Band	Height	Area (Data nm)
1	388	432.5	Blue	В	466.7	6787.440
2	413	438.0	Blue	В	458.3	6763.271
3	409	430.7	Blue	В	407.0	6327.327
4	427	442.4	Blue	В	462.4	6587.791
5	425	447.0	Blue	В	465.0	7513.319
6	435	459.5	Blue	В	483.2	7971.241



Fig. 1. (a) UV-vis; (b) fluorescence spectra of 1 (\_\_\_\_\_) and 6 (----).

strong charge-transfer absorption from ligand  $\pi$ -orbital to vacant titanium orbital (ligand to metal charge-transfer, LMCT bands) which are strongly affected by the chemical nature of the ligands giving colours to the complexes [15]. The electronic and fluorescence spectra of complexes **1** and **6** are given in Fig. 1. In fluorescence spectra of all the complexes one B band in blue region is observed. The data (Table 2) indicated them to behave like a fluorescent material.

# 3.2. Infrared spectra

In infrared spectra of all the complexes, the characteristic  $\nu$ (C=O) and  $\delta$ (O-H) of free carboxylic acids at 1710 cm<sup>-1</sup> and 935 cm<sup>-1</sup>, respectively, were found absent. The O-H stretching vibration of free hydroxyl group of hydroxycarboxylic acid was noticed at ~3400 cm<sup>-1</sup> in the spectra of the complexes, which indicated that the hydroxyl group of hydroxycarboxylic acid was not bound to titanium and remained free. Two strong bands were observed in the range 1592–1545 cm<sup>-1</sup> and 1460–1435 cm<sup>-1</sup> which could be assigned due to ( $\nu_{asym}$ OCO) (antisymmetric) and ( $\nu_{sym}$ OCO) (symmetric) vibrations of the carboxylate ions, respectively [16]. The differences between the symmetric and

antisymmetric stretches,  $\Delta$  [ $\nu_{asym}$ OCO –  $\nu_{sym}$ OCO] were found in the range 110–132 cm<sup>-1</sup>. This indicated that carboxylate groups of both palmitic acid and hydroxycarboxylic acids were coordinated to titanium in a bidentate chelating mode involving coordination of both the oxygen atoms of –COOH group [16]. No band was found in 1626–1700 cm<sup>-1</sup> region indicating the CO group of acetylacetone was not free in the complexes. Two splitted new bands observed at ~1615 cm<sup>-1</sup> ( $\nu$ C === 0) and ~1530 cm<sup>-1</sup> ( $\nu$ C === C) indicated the chelating nature of acetylacetonate ion in the complexes [17]. The bands around 670 and 465 cm<sup>-1</sup> could be assigned to ring deformation  $\nu_{Ti-O}$  and  $\nu_{Ti-O}$  vibrations, respectively [16]. A representative infrared spectrum of complex **1** is given in Fig. 2.

#### 3.3. Hydrolytic stability of the complexes

The complex  $[Ti(acac)Cl_2(OOCC_{15}H_{31})]$  (**B**) is moisture sensitive [9]. Its sensitivity towards hydrolysis is reduced by substituting chloride ions by hydroxycarboxylic acids. This stability was tested by dissolving the complexes in benzene and 1% water was added and stirred the contents for 14 h open in the air. Following correlation in the hydrolytic stability may be sought: **1**, **3**, **5** < **2**, **4**, **6**.

Table 3

<sup>1</sup>H NMR spectral data ( $\delta$ , ppm) for titanium(IV) complexes.

Complex	<sup>1</sup> H
2	0.90 [s, 3H, CH <sub>3</sub> ], 1.27 [s, 26H, (–CH <sub>2</sub> ) <sub>13</sub> ], 1.64 [t, 2H, α-CH <sub>2</sub> ], 2.06 [s, 6H, acac], 5.63 [s, 1H, CH, acac], 7.68–6.79 [m, 8H, arom], 10.04 [s, 2H, OH, PhOH]
3	0.89 [s, 3H, CH <sub>3</sub> ], 1.26 [s, 26H, (-CH <sub>2</sub> ) <sub>13</sub> ], 1.64 [t, 2H, α-CH <sub>2</sub> ], 2.06 [s, 6H, acac], 5.60 [s, 1H, CH, acac], 5.23 [s, 1H, OH, -HCOH], 7.58–6.97 [m, 5H, arom]
4	0.90 [s, 3H, CH <sub>3</sub> ], 1.26 [s, 26H, (-CH <sub>2</sub> ) <sub>13</sub> ], 1.65 [t, 2H, α-CH <sub>2</sub> ], 2.06 [s, 6H, acac], 5.60 [s, 1H, CH, acac], 5.26 [s, 2H, OH, -HCOH], 7.59–6.81 [m, 10H, arom]
5	0.89 [s, 3H, CH <sub>3</sub> ], 1.27 [s, 26H, (-CH <sub>2</sub> ) <sub>13</sub> ], 1.64 [t, 2H, α-CH <sub>2</sub> ], 2.05 [s, 6H, acac], 5.63 [s, 1H, CH, acac], 5.37 [s, 1H, OH, -COH], 7.61–6.94 [m, 10H, arom]
6	0.89 [s, 3H, CH <sub>3</sub> ], 1.27 [s, 26H, (-CH <sub>2</sub> ) <sub>13</sub> ], 1.64 [t, 2H, α-CH <sub>2</sub> ], 2.06 [s, 6H, acac], 5.64 [s, 1H, CH, acac], 5.38 [s, 2H, OH, -COH], 7.61–6.72 [m, 20H, arom]



# 3.4. <sup>1</sup>H NMR spectra

In <sup>1</sup>H NMR spectrum of **1** (Fig. 3) a singlet was appeared at  $\delta = 0.89 \text{ ppm} (3\text{H})$  corresponding to methyl protons of palmitate ion [-OOCCH<sub>2</sub>(CH<sub>2</sub>)<sub>13</sub>CH<sub>3</sub>] and a singlet at  $\delta = 1.26 \text{ ppm}$  due to 26H of 13-CH<sub>2</sub> groups. A peak at  $\delta = 1.64 \text{ ppm} (2\text{H})$  indicated the  $\alpha$ -CH<sub>2</sub> protons of palmitate ion. A singlet at  $\delta = 2.05 \text{ ppm} (6\text{H})$  indicated the methyl protons of acetylacetonate ion while its methine proton was observed as a singlet at  $\delta = 5.62 \text{ ppm} (1\text{H})$ . A multiplet from  $\delta$  7.65 ppm to 6.88 ppm corresponded to aromatic ring protons of hydroxycarboxylate anion while the free hydroxyl proton attached to the ring appeared at  $\delta = 10.02 \text{ ppm}$ . The signal positions observed in the spectra for other complexes are given in Table 3.

#### 3.5. Powder XRD and TEM studies

Powder XRD was done for all the complexes which show first order reflection. The pattern and results of XRD suggested that the crystals of the complexes are not perfect but lying in between amorphous and crystalline character. Due to this reason, the complexes were not found suitable for single crystal XRD. A representative spectrum of complex **1** is given in Fig. 4. In this case, first order reflection occurs at 5.05° for (100) face, 12.71° for (010) face and 20.49° for (001) face. Using Bragg's equation, it can be shown that relative spacing between planes of the faces (100), (010) and (001) are 8.69 Å, 3.50 Å and 2.21 Å, respectively. Values of the unit cell dimensions are *a* = 8.69 Å, *b* = 3.50 Å and *c* = 2.21 Å. The data obtained can be attributed to the fact that

 $a \neq b \neq c$  and  $\alpha \neq \beta \neq \gamma \neq 90^{\circ}$ .

#### Table 4

Powder XRD structural data for complex 1.

1
TiC <sub>28</sub> H <sub>43</sub> O <sub>7</sub> Cl
Triclinic
Primitive
P1
8.69
3.50
2.21
5.05
12.71
20.49
8.69
3.50
2.21
337



Fig. 5. TEM image of 1.

This clearly indicates that the complex has some definite arrangements of structural units in a triclinic fashion. The structural parameters have been evaluated for complex **1** following the literature procedure [18] and given in Table 4.

Crystallite size for the complexes was calculated using maximum intensity peak by the standard Scherrer equation [19].

$$D = \frac{K\lambda}{(\beta\cos\theta)}$$

where *D* is the crystallite size; *K* is a constant (=0.94);  $\lambda$  is X-ray wavelength ( $\lambda$  = 1.5406 Å);  $\theta$  is Bragg diffraction angle and  $\beta$  is integral peak width which is converted into radian while calculation. The values obtained were in the range 136–185 nm.

The morphology of complex **1** was observed to have spherical particles (Fig. 5) of  $\sim$ 200 nm average diameter.

#### 4. Conclusions

Designing of a novel type of mononuclear, non-oxo, mixedligand complexes of titanium(IV) containing different ligands around the metal has been made which have spherical shaped particles. These complexes are semi-crystalline. They show fluorescent

#### Acknowledgements

Authors are thankful to the CSIR [no. 01(2293)/09/EMR-II] and [no. 09/057/(0200)/2010/EMR-I], and UGC [F. no. 37-132/2009 (SR)], New Delhi for financial support. They also thank CDRI, Luc-know for spectral and microanalysis.

### References

- [1] (a) G. Asgedom, A. Sreedhara, J. Kivikoski, J. Valkonen, E. Kolehmainen, C.P. Rao, Inorg. Chem. 35 (1996) 5674–5683;
  - (b) G. Asgedom, A. Sreedhara, J. Kivikoski, E. Kolehmainen, C.P. Rao, J. Chem. Soc. Dalton Trans. (1996) 93–97;
  - (c) G. Asgedom, A. Sreedhara, J. Kivikoski, C.P. Rao, Polyhedron 16 (1997) 643-651;
  - (d) C.P. Rao, A. Sreedhara, P.V. Rao, B.M. Verghese, K. Rissanen, E. Kolehmainen, N.K. Lokanath, M.A. Sridhar, J.S. Prasad, J. Chem. Soc. Dalton Trans. (1998) 2383–2394;

(e) C.P. Rao, A. Sreedhara, P.V. Rao, N.K. Lokanath, M.A. Sridhar, J.S. Prasad, Polyhedron 18 (1998) 289–297;

(f) L.F. Cui, D.M. Li, J.F. Wu, X.B. Cui, T.G. Wang, J.Q. Xu, J. Mol. Struct. 797 (2006) 34–39.

[2] (a) A. Cuin, A.C. Massabni, C.Q.F. Leite, J. Inorg. Biochem. 101 (2007) 291–296;

(b) Y. Qiu, K. Wang, Y. Liu, H. Deng, F. Sun, Y. Cai, Inorg. Chim. Acta 360 (2007) 1819–1824;

(c) W.X. Li, Y.S. Zheng, X.J. Sun, W.J. Chai, T. Ren, X.Y. Shi, J. Lumin. 130 (2010) 1455–1462;

(d) A.R. Abreu, M. Lourenco, D. Peral, M.T.S. Rosado, M.E.S. Eusebio, O. Palacios, J.C. Bayon, M.M. Pereira, J. Mol. Catal. A: Chem. 325 (2010) 91–97.

- [3] (a) D.C. Bradley, C.E. Holloway, J. Chem. Soc. A (1969) 282-285;
- (b) P.V. Rao, C.P. Rao, E.K. Wegelius, E. Kolehmainen, K. Rissanen, J. Chem. Soc. Dalton Trans. (1999) 4469–4474;
- (c) P.V. Rao, E. Kolehmainen, C.P. Rao, Ind. J. Chem. 41A (2002) 284–289. [4] (a) A.L. Allred, D.W. Thompson, Inorg. Chem. 7 (1968) 1196–1201;

(b) A.F. Lindmark, R.C. Fay, Inorg. Chem. 14 (1975) 282–287;
 (c) P. Comba, H. Jakob, B. Nuber, B.K. Keppler, Inorg. Chem. 33 (1994) 3396–3400.

- [5] (a) R.A. Lal, S. Bhaumik, A. Lemtur, M.K. Singh, D. Basumatari, S. Choudhury, A.K. De, A. Kumar, Inorg. Chim. Acta 359 (2006) 3105–3110;
  (b) R. Carballo, B. Covelo, N. Fernandez-Hermida, E. Garcia-Martinez, A.B. Lago, E.M. Vazquez-Lopez, Cryst. Growth Des. 8 (2008) 995–1004;
  (c) D. H. Carballo, B. Covelo, N. Fernandez-Hermida, E. Garcia-Martinez, A.B. Lago, E.M. Vazquez-Lopez, Cryst. Growth Des. 8 (2008) 995–1004;
- (c) P. Halder, E. Zangrando, T.K. Paine, Polyhedron 29 (2010) 434–440.
  [6] (a) Q. Zhou, H. Zhang, Y. Wang, X. Zhou, Spectrochim. Acta Part A 72 (2009) 110–114;

(b) X. Chen, Q. Wei, Y. Cai, Y. Han, Y. Zhao, B. Du, Spectrochim. Acta Part A 72 (2009) 1047–1053;

- (c) K.S. Jeon, T.S. Park, Y.D. Suh, M. Yoon, J. Photochem. Photobiol. A: Chem. 207 (2009) 20–27.
- [7] J.P. Corden, W. Errington, P. Moore, M.G. Partridge, M.G.H. Wallbridge, Dalton Trans. (2004) 1846–1851.
   [8] (a) K.L. Yeung, A.J. Maira, J. Stolz, E. Hung, N.K.C. Ho, A.C. We, J. Soria, K.J. Chao,
- [6] (d) K.L. Yeung, A.J. Maira, J. Stotz, E. Hung, N.K.C. HO, A.C. We, J. Sona, K.J. Chao, P.L. Yue, J. Phys. Chem. B 106 (2002) 4608–4616;
   (b) R. Uppal, C.D. Incarvito, K.V. Lakshmi, A.M. Valentine, Inorg. Chem. 45 (2006) 1795–1804.
- [9] B.P. Baranwal, T. Fatma, A.K. Singh, A. Varma, Inorg. Chim. Acta 362 (2009) 3461–3464.
- [10] (a) K. Strohfeldt, M. Tacke, Chem. Soc. Rev. 37 (2008) 1174–1187;
   (b) S. Gomez-Ruiz, B. Gallego, Z. Zizak, E. Hey-Hawkins, Z.D. Juranic, G.N. Kaluderovic, Polyhedron 29 (2010) 354–360.
- [11] W.L.F. Armarego, D.D. Perrin, Purification of Laboratory Chemicals, fourth ed., Butterworth-Heinemann, 1997.
- [12] G.H. Jeffery, J. Bassett, J. Mendham, R.C. Denney, Vogel's Textbook of Quantitative Inorganic Analysis, fifth ed., ELBS, England, 1997.
- [13] N. Serpone, P.H. Bird, A. Somogyvari, D.G. Bickley, Inorg. Chem. 16 (1977) 2381–2386.
- [14] W.J. Geary, Coord. Chem. Rev. 7 (1) (1971) 81-122.
- [15] B.N. Figgis, M.A. Hitchman, Ligand Field Theory and Its Applications, Wiley, New York, 2000.
- [16] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B, fifth ed., Wiley, New York, 1997.
- [17] M.K. Sharma, A. Singh, R.C. Mehrotra, Ind. J. Chem. 40 (2001) 568-572.
- [18] M.M. Woolfson, An Introduction to X-ray Crystallography, students ed, Cambridge University Press, 1980.
- [19] C.X. Quan, L.H. Bin, G.G. Bang, Mater. Chem. Phys. 91 (2005) 317-324.