

Available online at www.sciencedirect.com



SPECTROCHIMICA ACTA PART A

Spectrochimica Acta Part A 64 (2006) 637-641

www.elsevier.com/locate/saa

# Spectral characterization of iron(III) complexes of 2-benzoylpyridine N(4)-substituted thiosemicarbazones

Marthakutty Joseph, Anandaram Sreekanth, V. Suni, M. R. Prathapachandra Kurup\*

Department of Applied Chemistry, Cochin University of Science and Technology, Kochi 682 022, Kerala, India Received 11 April 2005; accepted 29 July 2005

#### Abstract

Three iron(III) complexes (1–3) of 2-benzoylpyridine N(4)-phenyl thiosemicarbazone (HL<sup>1</sup>) and one iron(III) complex (4) of 2-benzoylpyridine N(4)-cyclohexyl thiosemicarbazone (HL<sup>2</sup>) were synthesized and characterized by means of different physicochemical techniques viz., molar conductivity measurements, magnetic susceptibility studies and electronic, infrared and EPR spectral studies. The analytical data and the molar conductance measurements of the complexes reveal that two molecules of the ligand and the anion are coordinated to the metal atom in all the four complexes. The magnetic moments of the complexes suggest that they are of low spin. From the infrared spectra of the ligands and the complexes it is confirmed that the ligands coordinate to iron(III) as an anion coordinating via the azomethine nitrogen, pyridyl nitrogen, and the thiolate sulphur. The EPR spectra of the complexes in the polycrystalline state at 298 and 110 K and in DMF solution at 110 K were recorded and all the spectra show three g values indicating that these complexes have rhombic distortion. All the iron(III) complexes in DMF solution at 110 K have similar anisotropic spectra with almost the same  $g_{av}$  values, indicating that the bonding in all the complexes is similar and is unaffected by the coordination of the anion.

© 2005 Elsevier B.V. All rights reserved.

Keywords: 2-Benzoylpyridine; EPR spectra; Infrared spectra; Solid state reflectance spectra; Thiosemicarbazone

## 1. Introduction

Thiosemicarbazones and their metal complexes exhibit a wide range of biological applications. Owing to the interest they generate in pharmacology [1,2], thiosemicarbazones and their metal complexes have been extensively studied. The biological activity of thiosemicarbazones results from their ability to form chelates with metal ions. Thiosemicarbazones exist in the tautomeric thione (A) and thiol (B) forms (Fig. 1). The thione form acts as a neutral bidentate ligand while the thiol form deprotonates and acts as an anionic ligand [3]. There are some reports on the studies of N(4)-substituted 2-benzoylpyridine thiosemicarbazones and their metal complexes [4–6]. We have reported spectral and structural studies of copper(II) and iron(III) complexes of 2-benzoylpyridine N(4), N(4)-(butane-1,4-diyl) thiosemicarbazone [7,8]. Spectral characterization and crystal structure of 2-benzoylpyridine N(4)-cyclohexyl thiosemicarbazone [9] and its copper(II)

1386-1425/\$ - see front matter © 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2005.07.067

complexes are also reported [10]. As a part of our study of NNS donor ligands and their metal complexes [11–13], we now report the spectral characterization of the iron(III) complexes of two N(4)-substituted thiosemicarbazones derived from 2-benzoylpyridine.

## 2. Experimental

#### 2.1. Physical measurments

Carbon, hydrogen and nitrogen analyses of the ligands and the complexes were done on a Heraeus elemental analyzer at CDRI, Lucknow, India. The IR spectra were recorded on a Shimadzu DR 8001 series FTIR instrument using KBr pellets in the range 400–4000 cm<sup>-1</sup> and far IR spectra were recorded in the range 50-500 cm<sup>-1</sup> on a Nicolet Magna 550 FT-IR spectrometer using polyethylene pellets at RSIC, IIT, Bombay, India. The solid state electronic spectra of the ligands and their complexes were recorded in the 250–900 nm range in a diffused reflectance mode using MgO matrix on Ocean Optics SD2000 Fiber Optic Spectrometer. Electronic spectra of the ligands and the complexes in DMF solution were recorded on Shi-

<sup>\*</sup> Corresponding author. Tel.: +91 484 2575804; fax: +91 484 2577595. *E-mail address:* mrp@cusat.ac.in (M.R.P. Kurup).



Fig. 1. Thione-thiol tautomers of thiosemicarbazones.

madzu 160A UV–Visible spectrophotometer. The EPR spectra of the complexes were recorded on a Varian E-112 Spectrometer using TCNE as the standard and on a Bruker ESP300 X-band CW EPR spectrometer operating at 9.52 MHz equipped with a liquid nitrogen cryostat with the modulation amplitude of 0.05 mT and 100 kHz modulation frequency, and the field was calibrated by using 2,2-diphenyl-1-picrylhydrazyl (DPPH) with a *g* value of 2.0036. The magnetic susceptibility measurements were carried out at Indian Institute of Technology, Roorkee, India at room temperature in the polycrystalline state on a PAR model 155 Vibrating Sample Magnetometer at 5 K Oersted field strength. The molar conductances of the complexes of the solutions in dimethylformamide ( $10^{-3}$  M) at room temperature were measured using a direct reading conductivity meter.

#### 2.2. Synthesis of ligands

2-Benzoylpyridine N(4)-phenylthiosemicarbazone (HL<sup>1</sup>) was synthesized as follows [14]. Phenyl isothiocyanate 5.9 ml (50 mmol) in 50 ml methanol and hydrazine hydrate 2.4 ml (50 mmol) in 50 ml methanol were mixed with constant stirring. The resulting solution was kept in stirred condition for 0.5 h. The white product, *N*-phenylthiosemicarbazide formed was washed with methanol, and dried. 8.35 g (50 mmol) of *N*-phenylthiosemicarbazide was dissolved in 100 ml methanol. To this solution, a methanolic solution of 2-benzoylpyridine, 9.16 g (50 mmol) and two or three drops of acetic acid were added and refluxed for 5 h. The dark brown crystals, separated on cooling, were washed with methanol, recrystallized from ethanol and dried over P<sub>4</sub>O<sub>10</sub> in vacuo m.p. 135 °C.

2-Benzoylpyridine N(4)-cyclohexylthiosemicarbazone (HL<sup>2</sup>) were synthesized as reported previously [9]. The molecular structures of the ligands are shown in Fig. 2.



Fig. 2. Molecular structures of the ligands  $HL^1$  and  $HL^2$ .

### 2.3. Synthesis of complexes

Ethanolic solutions of ferric nitrate Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (1 mmol) and  $HL^{1}$  (2 mmol) were mixed and refluxed for 8 h to prepare  $[Fe(L^1)_2NO_3] \cdot 2H_2O(1)$ . The brown shining solids separated on keeping the solution for 2 days were filtered, washed with hot water, hot ethanol and ether and dried over  $P_4O_{10}$  in vacuo. [Fe( $L^1$ )<sub>2</sub>Cl] (2) and [Fe( $L^2$ )<sub>2</sub>NO<sub>3</sub>]·C<sub>2</sub>H<sub>5</sub>OH (4) were prepared by similar methods using the appropriate thiosemicarbazone and ferric chloride and ferric nitrate, respectively. Compound **3**,  $[Fe(L^1)_2NCS]$  was prepared by a metathetical displacement of the chloride anion of the ferric chloride complex by the addition of 1 mmol methanolic solution of KCNS to the reaction mixture containing HL<sup>1</sup> (2 mmol) and ferric chloride (1 mmol) in methanol. The resulting solution was refluxed for 4 h and kept overnight. The black crystals, which separated were filtered, washed with methanol and ether and dried over  $P_4O_{10}$ in vacuo.

## 3. Results and discussion

#### 3.1. Analytical measurements

The colors, stoichiometries, elemental analyses, and magnetic moments of the Fe(III) complexes are given in Table 1. The analytical data calculated for the four iron(III) complexes reveal the 1:2:1 stoichiometry for iron, thiosemicarbazone and gegenion. All the iron(III) complexes are found to be insoluble in methanol, ethanol, acetone and chloroform, but soluble in dimethylformamide and in dimethylsulphoxide. The molar conductivity measurements of all the complexes in DMF ( $10^{-3}$  M solution) have values in the range 30-50 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, which are consistent with their non-electrolytic nature [15]. This indicates that the anions are associated in the first coordination sphere of Fe(III).

### 3.2. Magnetic susceptibilities

High spin Fe(III) complexes in general, have magnetic moments at room temperature very close to the spin only value of 5.9 BM because the ground state (derived from the <sup>6</sup>S state of free ion) has no orbital angular momentum and there is no effective mechanism for introducing any coupling with the excited state. The low-spin complexes with  $t_{2g}^5$  configurations, usually have considerable orbital contribution to their magnetic moments and at room temperature the magnetic moment value is ~2.3 BM [16]. The magnetic moments of the synthesized iron(III) complexes in the polycrystalline state at room temperature are found to be in the range of 1.98–2.49 BM. These  $\mu_{eff}$  values fall in the range of those of low-spin iron(III) complexes [17].

#### 3.3. Infrared spectra

The tentative infrared spectral assignments of the ligands  $HL^1$  and  $HL^2$  and their Fe(III) complexes are given in Table 2. The  $\nu$ (C=N) bands of  $HL^1$  and  $HL^2$  are found at 1591 and 1582 cm<sup>-1</sup>, respectively. These strong bands are shifted after

Compound	Empirical formula	Color	Analytical data, found (calculated) (%)			μ (BM) at 300 K	Λ <sup>a</sup> M (in DMF)
			С	Н	N		
$\overline{\left[\operatorname{Fe}(\mathrm{L}^{1})_{2}\operatorname{NO}_{3}\right]}\cdot 2\operatorname{H}_{2}\operatorname{O}\left(1\right)$	C <sub>38</sub> H <sub>34</sub> N <sub>9</sub> S <sub>2</sub> O <sub>5</sub> Fe	Brown	56.57 (55.89)	4.41 (4.16)	15.07 (15.44)	2.2	35.6
$[Fe(L^1)_2Cl]$ (2)	C38H30N8S2ClFe	Blue	60.91 (60.53)	4.11 (3.98)	14.60 (14.86)	2.49	31.2
$[Fe(L^1)_2NCS]$ (3)	C39H30N9S3Fe	Black	60.01 (60.32)	4.09 (3.87)	16.04 (16.24)	1.98	42.6
$[Fe(L^2)_2NO_3].C_2H_5OH(4)$	$C_{40}H_{48}N_9S_2O_4Fe$	Brown	56.95 (57.29)	5.62 (5.73)	15.16 (15.04)	2.0	49.9

Table 1 Analytical data, color and magnetic moments of Fe(III) complexes

<sup>a</sup> Molar conductivity in ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> at 298 K using 10<sup>-3</sup> M solution.

Table 2

IR spectral assignments (cm<sup>-1</sup>) of HL<sup>1</sup> and HL<sup>2</sup> and its Fe(III) complexes

Compound	ν(C=N)	v(N-N)	ν(CS)	$\rho(py)$	v(Fe—N)	v(Fe-N)py	v(Fe-S)
HL <sup>1</sup>	1591 s	1102 s	835	622 m	_	_	_
$[Fe(L^1)_2NO_3] \cdot 2H_2O^a(1)$	1546 s	1125 m	752 m	665 m	492 s	363 s	442 s
$[Fe(L^1)_2Cl(2)]$	1566 s	1123 s	756 s	659 m	491 s	368 s	455 s
$[Fe(L^1)_2NCS]$ (3)	1562 s	1118 m	766 s	638 w	495 s	370 s	451 s
$HL^2$	1582	1118 s	833 m	607 m	_	_	_
$[Fe(L^2)_2NO_3] \cdot C_2H_5OH^b$ (4)	1546 s	1153 m	744 m	641 w	482 s	368 s	454 s

<sup>a</sup>  $\nu$ (NO<sub>3</sub>): 1492, 1384 cm<sup>-1</sup>.

<sup>b</sup>  $\nu$ (NO<sub>3</sub>): 1439, 1319 cm<sup>-1</sup>.

coordination towards lower energies by ca.  $30 \,\mathrm{cm}^{-1}$ , indicating coordination via azomethine nitrogen [18]. The  $\nu$ (N–N) bands of the thiosemicarbazones are found at 1102 and  $1118 \,\mathrm{cm}^{-1}$ . The increase in frequency of this band in the spectra of the complexes is an evidence for the enolization of the ligand and the coordination via the azomethine nitrogen. The bands observed at 835 and  $833 \text{ cm}^{-1}$  for HL<sup>1</sup> and HL<sup>2</sup>, respectively, are assigned to  $\nu$ (C=S). These bands are found to be shifted to low energies in the spectra of the complexes, indicating coordination via the thiolate sulfur [3,11]. The out-of-plane pyridine ring deformation modes of the free ligands at 622 and  $607 \,\mathrm{cm}^{-1}$  are found to be shifted to higher energies in the spectra of the complexes indicating coordination via the nitrogen atom of the pyridine ring [19]. The coordination positions of the thiosemicarbazones in the iron(III) complexes are confirmed by assigning the strong bands observed in the far IR spectra of the complexes as suggested by Nakamoto [20]. The strong bands observed at  $363-370 \text{ cm}^{-1}$  are assigned to v(Fe-N) of the pyridine ring. Another v(Fe-N) band is observed at 482-495 cm<sup>-1</sup> in the spectra of the Fe(III) complexes indicating  $\nu$ (Fe–N) of the azomethine group. Again the strong bands observed in the region 442-455 cm<sup>-1</sup> are assigned to the v(Fe-S) bond. The iron-chlorine stretching band is normally observed between 300 and  $200 \text{ cm}^{-1}$  [21]. A strong band at  $255 \text{ cm}^{-1}$  in the chloro complex confirms the coordination of the chloride ion to Fe(III).

The IR spectrum of  $[Fe(L^1)_2NO_3]\cdot 2H_2O$ , which exhibits two bands at 1439 and 1319 cm<sup>-1</sup> corresponds to the NO stretching bands of the nitrate ion. The separation of these bands by  $120 \text{ cm}^{-1}$  indicates the unidentate nature of the nitrate ion in the complex [22]. According to Stefov et al. [23] coordinated water should exhibit frequencies at 825, 575 and 500 cm<sup>-1</sup>. The absence of spectral bands in these regions in the spectrum of this complex indicates that the water molecules in  $[Fe(L^1)_2NO_3]\cdot 2H_2O$  are not coordinated, but exist as lattice water. Similarly, the bands at 1492 and  $1384 \text{ cm}^{-1}$  in the spectrum of [Fe (L<sup>2</sup>)<sub>2</sub>NO<sub>3</sub>]·C<sub>2</sub>H<sub>5</sub>OH confirm the terminal unidentate coordination of the nitrate ion to Fe(III) in the complex.

## 3.4. Electronic spectra

The electronic absorption bands recorded in the polycrystalline state of the iron(III) complexes are given in Table 3. The bands observed at ca. 277 and 335 nm can be assigned to the  $\pi \to \pi^*$  and  $n \to \pi^*$  transitions of the thiosemicarbazones. Usually  $n \to \pi^*$  transitions occur at a lower energy than  $\pi \to \pi^*$ transitions. Two broad absorption bands are present in the region 656–400 nm. They are charge transfer transitions due to  $d \to \pi^*$ metal-to-ligand and S  $\to$  Fe(III) electronic transitions [24–26]. Because of the greater oxidizing power of Fe(III), ligand-metal charge transfer bands often obscure the very low intensity, spin forbidden, d-d absorption bands [27]. In the spectra of iron(III) complexes, the shoulders that appeared at ca. 890 nm are due to  $d \to d$  transitions.

#### 3.5. Electron paramagnetic resonance spectra

The X-band CW-EPR spectra of the iron(III) complexes in the polycrystalline state were recorded at temperatures 110 and 298 K and in DMF solution at 110 (Fig. 3). The EPR spec-

Table 3Electronic spectral data (nm) of Fe(III) complexes

Compound	d–d	Charge transfer	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^{*}$
$[Fe(L^1)_2NO_3]\cdot 2H_2O(1)$	875 sh	656, 419	332	278
$[Fe(L^1)_2Cl](2)$	887 sh	655, 417	337	278
$[Fe(L^1)_2NCS(3)]$	884 sh	652, 408	330	280
$Fe(L^2)_2NO_3 \cdot C_2H_5OH(4)$	890 sh	650, 402	335	276



Fig. 3. X-band CW-EPR spectra of compounds 1 (top) and 2 (bottom) in DMF measured at 110 K. Experimental spectrum (Exp.), simulated spectrum (Sim.). Small signal on top is DPPH.

tral parameters are presented in Table 4. The spin Hamiltonian parameters of the complexes were obtained after the spectral simulations performed by EasySpin package [28]. The EPR spectrum of the  $d^5$  iron(III) is expressed by the spin Hamiltonian [29,30]:

$$\hat{H} = \beta[g_x H_x \cdot S_x + g_y H_y \cdot S_y + g_z H_z \cdot S_z] \quad \text{with}$$
$$S = \frac{1}{2} \text{ and } g = 2.00$$

Spectra of all complexes recorded at room temperature in polycrystalline state as well as a solution in DMF show three g values indicating rhombic distortion. There is little difference in the spectra obtained in frozen solution at 110 K and in the solid state indicating that the iron(III) centres do not undergo alteration in solution. The observed anisotropic character with three g values due to rhombic distortion is common for spin-paired iron(III) complexes [31]. The g values confirm the low–spin character of iron(III) as confirmed from the mag-

Table 4	
EPR spectral parameters of Fe(III) complexes	

Compound	State	Temperature (K)	<i>g</i> <sub>1</sub>	<i>g</i> <sub>2</sub>	<i>g</i> <sub>3</sub>
$\overline{[Fe(L^1)_2NO_3]\cdot 2H_2O(1)}$	Powder	298	2.045	2.128	2.180
	Powder	110	2.027	2.141	2.184
	DMF	110	2.001	2.14	2.18
$[Fe(L^1)_2Cl(2)]$	Powder	298	2.009	2.130	2.155
	Powder	110	2.003	2.149	2.184
	DMF	110	2.004	2.140	2.185
[Fe(L <sup>1</sup> ) <sub>2</sub> NCS ( <b>3</b> )	Powder	298	2.008	2.134	2.169
	DMF	110	2.005	2.127	2.166
$[Fe(L^2)_2NO_3] \cdot C_2H_5OH$ (4)	Powder	298	2.080	2.294	2.334
	Powder	110	2.017	2.173	2.209
	DMF	110	2.021	2.159	2.205

netic moment values. The anisotropic character with the three *g* values due to rhombic distortion is not uncommon for spinpaired iron(III) since this behavior has been reported for Schiff base as well as porphyrin Fe(III) complexes. The small deviation of the anisotropic *g* value from 2.0 suggests that the electronic structure of the ground state is  $(d_{xz})^2$ ,  $(d_{yz})^2$ ,  $(d_{xy})^1$  [8,32].

At 110 K, all the iron(III) complexes in DMF solution have similar anisotropic spectra with almost the same  $g_{av}$  values, indicating that the bonding in all the complexes is similar and is unaffected by the coordination of the anion.

Based on the physicochemical studies, all the iron(III) complexes are assigned either a capped octahedral or a pentagonal bipyramidal geometry [33]. EPR data also suggest that the iron(III) complexes are of low spin with the association of anions in the first coordination sphere of iron(III) in the solid state. In the capped octahedral structure two molecules of the ligand  $L^1$ or  $L^2$  can occupy the six corners of an octahedron and an additional position is occupied by an anion at one triangular face of this octahedron. In an alternate pentagonal bipyramidal structure [33], two molecules of the  $L^1$  or  $L^2$  can occupy two axial positions and four positions in the equatorial position plane, an additional fifth position in the equatorial plane being occupied by the anion.

The complexes prepared from 2-acetylpyridine thiosemicarbazones and FeCl<sub>3</sub> given in earlier reports were found to exist as an ion pair consisting of a low-spin iron cation center and high spin tetrachloroferrate anion with the composition [FeL<sub>2</sub>] FeCl<sub>4</sub>. The presence of high spin in these complexes is proved by an EPR signal at ca. 4.3 [8,26]. However, the absence of an EPR signal at 4.3 in the present complex **2** indicates exclusive presence of spin-paired iron(III) in conformity with the magnetic moment measurements.

#### Acknowledgments

The authors are indebted to the Regional Sophisticated Instrumentation Centre, CDRI, Lucknow, India and RSIC, IIT, Bombay, for analytical measurements. M. Joseph would like to thank Kerala State Council for Science, Technology and Environment, Government of Kerala for financial assistance.

## References

- [1] M.J.M. Campbell, Coord. Chem. Rev. 15 (1975) 279.
- [2] D.X. West, A.E. Liberta, S.B. Padhye, R.C. Chikate, P.B. Sonavane, A.S. Kumbhar, R.G. Yerande, Coord. Chem. Rev. 123 (1993) 49.
- [3] M.R.P. Kurup, M. Joseph, Synth. React. Inorg. Met.-Org. Chem. 33 (2003) 1275.
- [4] H. Beraldo, W. Nacif, A. Rebolledo, R. Costa, J.D. Ardisson, Brazilian Meeting on Inorganic Chemistry, 2002.
- [5] D.X. West, I.S. Billeh, J.P. Jesinski, J.M. Jesinski, R.J. Butcher, Transition Met. Chem. 23 (1998) 209.
- [6] D.X. West, N.M. Kozub, G.A. Bain, Transition Met. Chem. 21 (1996) 52.
- [7] A. Sreekanth, M.R.P. Kurup, Polyhedron 22 (2003) 3321.
- [8] A. Sreekanth, M.R.P. Kurup, Polyhedron 23 (2004) 969.
- [9] M. Joseph, V. Suni, C.R. Nayar, M.R.P. Kurup, H.K. Fun, J. Mol. Struct. 705 (2004) 63.

97.

- [10] M. Joseph, V. Suni, M.R.P. Kurup, M. Nethaji, A. Kishore, S.G. Bhat, Polyhedron 23 (2004) 3069.
- [11] V. Philip, V. Suni, M.R.P. Kurup, M. Nethaji, Polyhedron 23 (2004) 1225.
- [12] A. Sreekanth, H.K. Fun, M.R.P. Kurup, Inorg. Chem. Commun. 7 (2004) 1250.
- [13] A. Sreekanth, S. Sivakumar, M.R.P. Kurup, J. Mol. Struct. 655 (2003) 47.
- [14] D.L. Klayman, J.F. Bartosevich, T.S. Griffin, C.J. Mason, J.P. Scovill, J. Med. Chem. 22 (1979) 855.
- [15] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.
- [16] R.L. Dutta, A. Syamal, Elements of Magnetochemistry, second ed., East-West Press, New Delhi, 1993.
- [17] R. Raina, T.S. Srivastava, Indian J. Chem. 22A (1983) 701.
- [18] R.P. John, A. Sreekanth, V. Rajakannan, T.A. Ajith, M.R.P. Kurup, Polyhedron 23 (2004) 2549.
- [19] D.X. West, G. Ertem, M. Patricia, J.P. Scovill, D.L. Klayman, L. Judith, F. Anderson, R. Gillardi, C. George, L.K. Pannel, Transition Met. Chem. 10 (1985) 264.
- [20] K. Nakamoto, Infrared and Raman spectra of Inorganic and Coordination compounds, fifth ed., Wiley, New York, 1997.

- [21] R. Raina, T.S. Srivastava, Inorg. Chim. Acta 67 (1982) 83.
- [22] S.K. Jain, B.S. Garg, Y.K. Bhoon, Transition Met. Chem. 11 (1986) 89.
  [23] V. Stefov, V.M. Petrusevski, B. Soptrajanov, J. Mol. Struct. 293 (1993)
- [24] S. Burman, D.N. Sathyanarayana, Indian J. Chem. 20A (1981) 57.
- [25] B.S. Garg, M.R.P. Kurup, S.K. Jain, Y.K. Bhoon, Transition Met. Chem. 13 (1988) 247.
- [26] A. Sreekanth, H.K. Fun, M.R.P. Kurup, J. Mol. Struct. 737 (2005) 61.
- [27] A.B.P. Lever, Inorganic Electronic Spectroscopy, second ed., Elsevier Science Publishing Company, Amsterdam, 1984.
- [28] St. Stoll, Spectral simulations in solid-state EPR, Ph.D. thesis, ETH Zurich, 2003.
- [29] B. Bleaney, M.C.M. Obrein, Proc. Phy. Soc., London Sect. B69 (1956) 1216.
- [30] J.S. Griffith, The Theory of Transition Metal ions, Cambridge University Press, London, 1961.
- [31] Y. Nishida, A. Sumitha, K. Hayashida, H. Ohsima, S. Kida, Y. Maeda, J. Coord. Chem. 9 (1979) 161.
- [32] K. Nishida, O. Oshio, S. Kadia, Inorg. Chim. Acta 23 (1977) 59.
- [33] B.S. Garg, M.R.P. Kurup, S.K. Jain, Y.K. Bhoon, Synth. React. Inorg. Met.-Org. Chem. 28 (1998) 1415.