Thermochimica Acta, 240 (1994) 175–184
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(94)01685-A

Thermal studies of some transition metal complexes of phenylazoacetoacetanilide (HPAAC)

A.Y. Desai and A.D. Sawant *

Department of Chemistry, The Institute of Science, 15, Madam Cama Road, Bombay-400 032, India

(Received 30 July 1993; accepted 9 December 1993)

Abstract

Phenylazoacetoacetanilide complexes of the type $M(PAAC)_n$, where M is Cu(II), Ni(II), Co(II), Fe(II), Pd(II), VO(II) or UO_2(II), *n* is the valency of the metal, and HPAAC is phenylazoacetoacetanilide, have been synthesized and characterized. In these complexes, the phenylazo group ($C_6H_5N_2$) exhibits bidentate character and coordinates symmetrically with the metal through the phenylazo amd methylketone groups. Thermogravimetric studies indicate that there is an initial endothermic reaction followed by exothermic dissociation. The thermodynamic parameters and the order of reactions were calculated from the TG and DTA curves.

INTRODUCTION

The chemistry of aryldiazenato complexes is of recent origin. Many researchers have been intrigued by the chemistry of aryldiazenato complexes of various transitional metals because of their striking structural features and applications in diverse areas [1–5], most notably in dyes and pigment technology.

A survey of earlier investigations [6–10] shows that no thermal studies have been reported on the phenylazoacetoacetanilide complexes of Cu(II), Ni(II), Co(II), Fe(II), VO(II) and UO_2(II). The present paper describes the synthesis, characterization, and thermal decomposition studies of these complexes.

EXPERIMENTAL

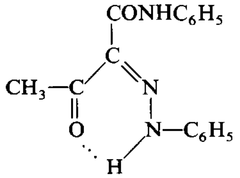
All reagents and chemicals used were of AR grade. The ligand phenylazoacetoacetanilide (HPAAC, Structure 1) was prepared by a standard method [11]. The crystallized ligand showed the expected elemental composition, and infrared and ^{1}H NMR spectra. Metal complexes were prepared

---

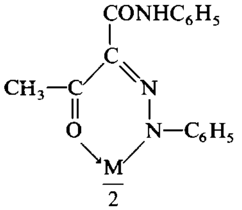
* Corresponding author.

0040-6031/94/$07.00 © 1994 – Elsevier Science B.V. All rights reserved

by slow addition of an alcoholic solution of the ligand to 100 cm^3 of an aalcoholic aqueous solution of the metal, in 1:2 molar ratio of metal to ligand. The pH of the solution was raised to an appropriate value and the precipitate formed was filtered, and washed with distilled water, and ethanol. It was then dried over P_2O_5 in a vacuum. Complexes were then subjected to thermal decomposition studies.



Structure 1. HPAAC, phenylazoacetoacetanilide.



Structure 2. Metal complex of HPAAC; M is Cu(II), Ni(II), Co(II), Fe(II), Pd(II), VO(II) or UO_2(II).

INSTRUMENTATION

Elemental analysis of the complexes was carried out by routine methods (Table 1). Molar conductance measurements were made in nitrobenzene at room temperature with 1 mM complex concentration, using an ELICO digital conductivity meter. Magnetic susceptibilities were recorded on Gauy's balance at 303 K. The IR spectra of the complexes and ligand were recorded in KBr on Beckman IR-20 and Perkin-Elmer IR spectrophotometers, in the range 4000–400 cm^{-1}. ^1H NMR spectra of the complex and ligand were recorded on a VXR 3005 Supercon FTNMR spectrometer using d_6-DMSO. Diffuse reflectance spectra were recorded on a 106 (MKII) Systronic spectrophotometer. The thermogravimetric analyses (TGA and DTA) were carried out in nitrogen atmosphere on a Shimadzu, DT-30 recording thermal analyser up to 800°C at a scan rate of 10°C min^{-1} with a chart speed of 2.5 mm min^{-1}.

RESULTS AND DISCUSSION

The elemental analyses (Table 1) confirm the assigned stoichiometries. All the complexes were found to be non-electrolytic in nature. Except for the palladium(II) complex, the complexes were found to be paramagnetic. The stereochemistries of the complexes were ascertained using magnetic studies, and diffuse reflectance, IR and ^1H NMR spectra. The ligand (HPAAC) showed broad bands at 2900 and 3200 cm^{-1} corresponding to ν(N–H) of the hydrazone group and ν(N–H) of the anilide groups, respectively [10]. The spectra of all the metal complexes lacked the 2900 cm^{-1} band, indicating replacement of a proton from the hydrazone group, whereas the band at 3200 cm^{-1} persisted suggesting non-involvement of the

TABLE 1

Physical and analytical data of HPAAC complexes

Reagent/metal complex and colour	Molar conductance $\Omega/cm^2\ mol^{-1}$	Molecular weight	pH of formation	μ_{eff} [a]/BM	Elemental analysis/% Found (calculated)			
					C	H	N	Metal
Reagent (HPAAC) $C_{16}H_{15}O_2N_3$ (Yellow)	–	281	–	–	68.88 (68.32)	5.72 (5.33)	14.21 (14.94)	– –
$Cu(C_{16}H_{14}O_2N_3)_2 \cdot 2H_2O$ (Green)	2.20	659.5	4.5	1.80	58.92 (58.22)	4.86 (4.85)	12.84 (12.73)	10.01 (9.62)
$Cu(C_{16}H_{14}O_2N_3) \cdot OCOCH_3$ (Green)	1.88	402.5	4.7	1.01	53.36 (53.66)	4.51 (4.22)	9.98 (10.43)	15.28 (15.77)
$Ni(C_{16}H_{14}O_2N_3)_2 \cdot 2H_2O$ (Light green)	4.20	654.5	5.8	3.2	58.93 (58.67)	4.50 (4.88)	13.08 (12.83)	8.88 (8.93)
$Co(C_{16}H_{14}O_2N_3)_2 \cdot 2H_2O$ (Brown)	4.60	654.9	6.7	5.20	58.63 (58.63)	4.88 (4.88)	12.85 (12.82)	9.02 (8.91)
$Fe(C_{16}H_{14}O_2N_3)_2 \cdot 2H_2O$ (Brown)	7.20	651.8	6.8	5.88	58.33 (58.91)	4.27 (4.90)	12.55 (12.88)	8.86 (8.56)
$Pd(C_{16}H_{14}O_2N_3)_2$ (Brown)	9.70	702.0	7.5	Diamagnetic	58.02 (57.65)	4.28 (4.20)	12.42 (12.61)	15.40 (15.91)
$VO(C_{16}H_{14}O_2N_3)_2$ (Green)	4.60	626.0	5.9	1.70	60.78 (61.34)	4.48 (4.47)	14.02 (13.41)	8.08 (7.98)
$UO_2(C_{16}H_{14}O_2N_3)_2$ (Yellow)	3.38	830.0	7.8	1.40	46.14 (46.26)	3.41 (3.37)	10.22 (10.12)	28.14 (28.68)

[a] At 303 K.

anilide group in bonding. The band at 1650 cm^{-1}, due to the $\nu(CH_3-C=O)$ group in the ligand spectra, was found to be shifted to lower values of 1620-1610 cm^{-1} in all the complexes, suggesting coordination through the oxygen atom of the $CH_3-C=O$ group. These coordination sites were corroborated by the presence of bands at 550 and 450 cm^{-1}, attributed to ν(M-N) and ν(M-O) bonding, respectively [12] (Table 2).

^1H NMR spectra of the ligand in d_6-DMSO showed two prominent down-field signals at δ -11.2 (s) ppm and δ -13.6 (s) ppm, attributed to the anilide N-H and hydrazone N-H protons, respectively, whereas ^1H NMR spectra of the complexes in d_6-DMSO lacked the signal at δ -13.6 ppm, but the signal at δ -11.2 ppm was not affected. Also, splitting of the $CH_3-C=O$ signal (δ -2.45 ppm) was observed, proving that coordination was taking place through the N-H of hydrazone and the oxygen atom of the $CH_3-C=O$ group. This coordination pattern of reagent HPAAC was analogous to that found for similar hydrozones reported by earlier workers [13]. The diffuse reflectance spectra of the complexes exhibited bands at around 360, 700 and 1100 mm which were ascribed to intra-ligand, metal-ligand and d-d transitions respectively [14]. All these experimental data suggest octahedral structures for the Cu(II), Ni(II), Co(II) and Fe(II) complexes, square-planar structures for the Pd(II) and Cu(II) acetate complexes, a square-pyramidal structure for the VO(II) complex, and a pentagonal-bipyramidal structure for the UO_2(II) complex.

THERMAL DECOMPOSITION OF THE COMPLEX

$Cu(PAAC)_2 \cdot 2H_2O$

The TG curve of this complex (Fig. 1, curve 1) reveals the loss of the water molecules at around 140°C. The presence of coordinated water molecules in the complex is supported by the IR and elemental analysis studies. The subsequent dissociation of the complex takes place, with loss of the phenylazo group at 220°C, followed by disintegration of the anilide and methylketone groups at 350°C. Above 400°C, the weight of the residue is almost constant, indicating complete decomposition. The DTA curve (Fig. 2, curve 1) indicates two endothermic peaks with T_{max} at 150 and 190°C; the peak at 350°C is exothermic. The decomposition was found to follow first-order kinetics and the activation energy was determined as 0.257 kcal mol^{-1}.

$Cu(PAAC) \cdot OCOCH_3$

The TG curve of this complex (Fig. 1, curve 6) reveals that decomposition starts at 400°C with fission of the phenylazo and acetate groups of the dimeric structure. This is followed by dissociation of the complex at 400°C, separat-

TABLE 2

Infrared spectral data of HPAAC and metal complexes of HPAAC in cm^{-1}

Complex	Coordinated water	ν_{str}(N–H) from hydrazino group	ν_{str}(C=O) from $CH_3C=O$ group	ν_{str}(C=O)	ν_{str}(O=U=O)	ν_{vib}(M–N)	ν_{vib}(M–O)
HPAAC	–	3100 3060(b)	1450(s)	1600(w)	–	–	–
$Cu(PAAC)_2 \cdot 2H_2O$	3450(m)	–	1610(s)	1590(w)	–	580(m)	480(m)
$Cu(PAAC) \cdot OCOCH_3$	–	–	1625(s)	1595(w)	–	580(m)	460(m)
$Ni(PAAC)_2 \cdot 2H_2O$	3460(m)	–	1620(s)	1595(w)	–	580(m)	480(m)
$Co(PAAC)_2 \cdot 2H_2O$	3460(m)	–	1630(s)	1600(w)	–	580(m)	440(m)
$Fe(PAAC)_2 \cdot 2H_2O$	3450(m)	–	1620(s)	1610(w)	–	570(m)	450(m)
$Pd(PAAC)_2$	–	–	1625(s)	1600(w)	–	570(m)	460(m)
$VO(PAAC)_2$	–	–	1620(s)	1590(w)	–	580(m)	490(m)
$UO_2(PAAC)_2$	–	–	1630(s)	1570(w) and 1590(m)	830(m) and 960(m)	580(m)	480(m)

Key: m, medium; s, strong; b, broad.

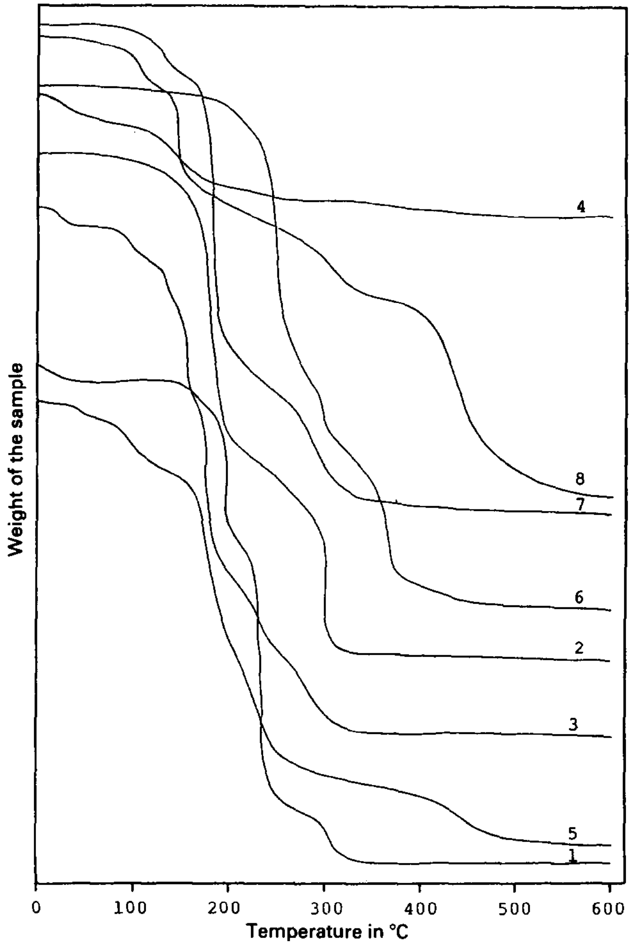


Fig. 1. TG curves of complexes of HPAAC: 1, Cu[PAAC]$_2 \cdot 2H_2O$; 2, VO[PAAC]$_2$; 3, Co[PAAC]$_2 \cdot 2H_2O$; 4, UO$_2$[PAAC]$_2$; 5, Ni[PAAC]$_2 \cdot 2H_2O$; 6, Cu[PAAC] · OAC; 7, Pd[PAAC]$_2$; 8, Fe[PAAC]$_2 \cdot 2H_2O$.

ing the anilide and methylketone groups. This continues up to 500°C at which temperature the weight of the residue remains nearly unchanged. The DTA curve (Fig. 2, curve 6) shows three exothermic peaks with T_{max} at 250, 390 and 400°C, respectively. The order of reaction and activation energy of the decomposition reaction were determined by the Freeman–Carroll equation and were found to be 0.8 and 0.328 kcal mol^{-1}, respectively.

Ni(PAAC)$_2 \cdot 2H_2O$

The TG curve of this complex (Fig. 1, curve 5) indicates loss of the water molecules at 120°C. Thereafter, dissociation of the complex occurs at a brisk rate up to 450°C, with loss of two phenylazo groups and also of the

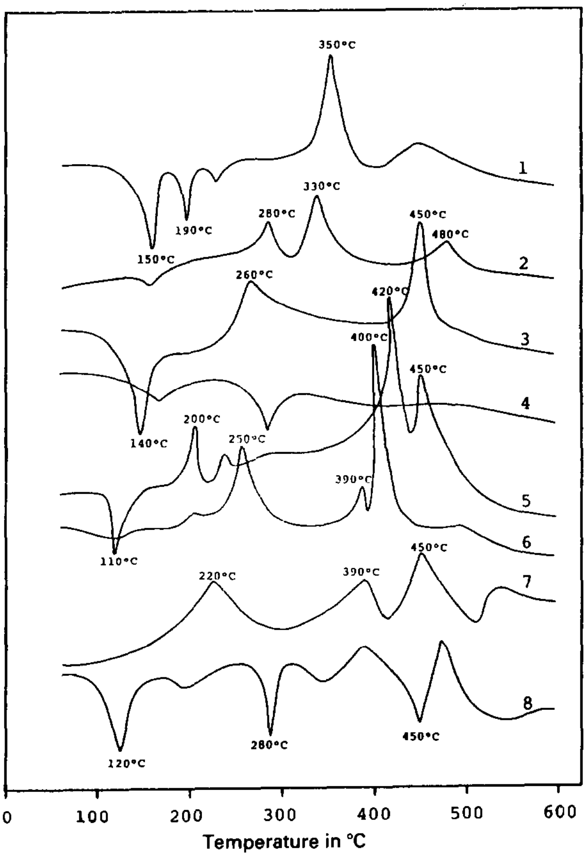


Fig. 2. DTA curves of complexes of HPPAC: 1, Cu[PAAC]$_2 \cdot 2H_2O$; 2, VO[PAAC]$_2$; 3, Co[PAAC]$_2 \cdot 2H_2O$; 4, UO_2[PAAC]$_2$; 5, Ni[PAAC]$_2 \cdot 2H_2O$; 6, Cu[PAAC] · OAC; 7, Pd[PAAC]$_2$; 8, Fe[PAAC]$_2 \cdot 2H_2O$.

outer anilide groups. The decomposition is nearly complete between 520 and 550°C, above which the weight of residue is almost unchanged. The DTA curve (Fig. 2, curve 5) first shows on endothermic peak with a T_{max} of 110°C, followed by three exothermic peaks of T_{max} 200, 420 and 450°C, respectively. The reaction was found to follow first-order kinetics, with an activation energy of 0.119 kcal mol^{-1}.

Co(PAAC)$_2 \cdot 2H_2O$

The TG curve of the Co(PAAC)$_2$ complex (Fig. 1, curve 3) shows that the decomposition begins with dehydration of the coordinated water molecules at 140°C followed by dissociation of the complex with loss of the phenylazo groups at 260°C. The decomposition is complete at 480°C after total loss of the anilide and other groups. Above 500°C, the weight of residue is unchanged. The DTA curve (Fig. 2, curve 3) exhibits one endothermic peak with a $T_{\max}$ of 140°C, corresponding to dehydration and two exothermic peaks with $T_{\max}$ 260 and 450°C. The order of reaction and activation energy of the decomposition were determined by the Freeman–Carroll equation as 1 and 0.196 kcal mol^{-1}, respectively.

$Fe(PAAC)_2 \cdot 2H_2O$

The TG curve of the $Fe(PAAC)_2$ complex (Fig. 1, curve 8) shows that the dehydration starts out around 120°C, accompanied by dissociation of the phenylazo groups up to 350°C. The decomposition is completed by the loss of the anilide groups at 600–650°C. Above this, the weight of the residue remains unchanged. The DTA curve (Fig. 2, curve 8) shows three endothermic peaks of $T_{\max}$ 120, 280 and 450°C, respectively. The order of the decomposition reaction was found to be 0.5; the activation energy was found to be 0.339 kcal mol^{-1}.

$Pd(PAAC)_2$

The TG curve of this complex (Fig. 1, curve 7) indicates that the decomposition of $Pd(PAAC)_2$ begins in the temperature range 220–230°C, separating the two $C_6H_5N_2$ groups. Then dissociation is observed at 390–450°C due to loss of two C_6H_5 groups and two CONH groups. Decomposition is completed on removal of two CH_3 groups in the temperature range 440–450°C. The complex shows three DTA peaks (Fig. 2, curve 7). All the peaks are exothermic in nature, with $T_{\max}$ values of 220, 390 and 450°C, respectively. The order of reaction and activation energy of the decomposition reaction were determined by the Freeman–Carroll equation as 0.6 and 0.497 kcal mol^{-1}, respectively.

$VO(PAAC)_2$

The TG curve of this complex (Fig. 1, curve 2) reveals that decomposition of the complex starts at 280°C, with dissociation of the phenylazo groups taking place around 330°C. This decomposition is accompanied by loss of the anilide groups which was complete at 480°C. After this, the weight of the residue remains unchanged. The DTA curve (Fig. 2, curve 2) showed three exothermic peaks with $T_{\max}$ at 280, 330 and 480°C. The order of the decomposition reaction and the activation energy were determined by the Freeman–Carroll equation as 0.9 and 0.283 kcal mol^{-1}, respectively.

$UO_2(PAAC)_2$

The uranyl complex was found to exhibit a simultaneous type of decomposition [15]. Therefore, the Freeman–Carroll equation could not be applied

TABLE 3

Thermal decomposition data

Complex	Temp. range/°C	Group decomposed	Observed (calculated) wt. loss/%	Enthalpy ΔH/kcal mol^{-1}
$Cu(PAAC)_2 \cdot 2H_2O$	140–170	$2H_2O$	5.27 (5.45)	$\Delta H_1 = 50.73$
	190–220	$2C_6H_5N_2$	36.97 (37.30)	$\Delta H_2 = 18.44$
	340–350	2CONH	77.35 (78.24)	$\Delta H_3 = -676.47$
$Cu(PAAC) \cdot OCOCH_3$	220–250	$2C_6H_2N_2$, $2CH_3CO \cdot O$	39.82 (40.14)	$\Delta H_1 = -357.70$
	390–410	$2C_6H_5$	59.41 (59.87)	$\Delta H_2 = -51.11$
	450–460	2CONH	74.88 (74.28)	$\Delta H_3 = -4374.50$
$Ni(PAAC)_2 \cdot 2H_2O$	120–150	$2H_2O$	5.28 (5.48)	$\Delta H_1 = -9.80$
	250–270	$2C_6H_5N_2$	36.72 (37.58)	$\Delta H_2 = -39.50$
	420–450	2CONH	74.52 (74.25)	$\Delta H_3 = -99.13$
	520–550	$2CH_3$	78.98 (78.83)	
$Co(PAAC)_2 \cdot 2H_2O$	140–170	$2H_2O$	5.31 (5.49)	$\Delta H_1 = 27.71$
	240–260	$2C_6H_5N_2$	37.17 (37.56)	$\Delta H_2 = -27.00$
	280–290	2CONH	50.44 (50.69)	
	410–430	$2C_6H_5$	73.44 (74.20)	$\Delta H_3 = -346.30$
	460–480	$2CH_3$	78.76 (78.79)	
$Fe(PAAC)_2 \cdot 2H_2O$	140–150	$2H_2O$	5.58 (5.52)	$\Delta H_1 = 640.93$
	330–340	$2C_6H_5N_2$	37.78 (37.74)	$\Delta H_2 = 39.20$
	440–450	2CONH	50.30 (50.90)	$\Delta H_3 = 235.30$
$Pd(PAAC)_2$	220	$2C_6H_5\,N_2$	31.43 (31.53)	$\Delta H_1 = -25.00$
	390–400	$2C_6H_5$, 2CONH	67.78 (67.56)	$\Delta H_2 = -83.30$
	440–450	$2CH_3$	71.98 (72.07)	$\Delta H_3 = -1000.00$
$VO(PAAC)_2$	260–280	$2C_6H_5N_2$ groups	33.38 (33.54)	$\Delta H_1 = -90.19$
	330	2CONH groups	47.08 (47.28)	$\Delta H_2 = -67.64$
	480	$2C_6H_5$	71.04 (71.88)	$\Delta H_3 = -631.30$

to study the decomposition of the complex. The residue above 800°C was found to be U_3O_8.

The results of the TG and DTA studies are given in Table 3. In almost all the cases, the DTA curves show one endothermic and two exothermic peaks. The endothermic peak is probably due to dehydration or partial volatilization of the metal chelate. The exothermic peaks are due to partial dissociation of the complex. The trend of the reactions of the complexes, suggesting the dehydration of coordinated water in the earlier stage and subsequent exothermic dissociation, is in accordance with earlier work on similar ligands such as phenylazoacetylacetone, phenylazobenzoyl acetone and phenylazoethylacetoacetate [15], and may be attributed to some delocalization of the π-bonding electron between the chelating agent and the metal atom. It was observed that the mechanism of the decomposition was not changed with change in temperature. In these cases, the fraction of weight decomposed versus temperature shows Arrhenius-type plots and these are used to calculate the order of reaction n and the activation energy E_a. The difference differential method of Freeman and Carroll [16] was used for evaluating the kinetic parameters from thermogravimetric data. The enthalpies of dissociation for each decomposition step were found by the method of Stepin et al. [17]. From the initial decomposition temperatures, the relative thermal stabilities of the complexes were deduced [18]:

$$\mathrm{Ni(PAAC)_2} < \mathrm{Fe(PAAC)_2} < \mathrm{Co(PAAC)_2} \approx$$
$$\mathrm{Pd(PAAC)_2} < \mathrm{Cu(PAAC)_2} < \mathrm{Cu(PAAC)\cdot OAC} < \mathrm{VO(PAAC)_2}$$

ACKNOWLEDGMENTS

The authors are grateful to Dr Ramchandran of I.I.T. and the late Dr S.B. Khatavkar of G.N. Khalsa College, Bombay, for helpful discussions. We also thank the authorities of R.S.I.C. and I.I.T. Bombay for providing instrumental facilities.

REFERENCES

1 A. Chakrovarty and K.C. Kalia, Inorg. Chem., 7 (1968) 2016.
2 R.B. King and M.B. Bisnette, J. Am. Chem. Soc., 86 (1964) 5694.
3 A.P. Gaughan, B.L. Haymore, J.A. Ibers, W.H. Myers, T.E. Neppier and W.W. Meak, J. Am. Chem. Soc., 95 (1973) 6859.
4 N.C. Connely and J.D. Davis, J. Organomet. Chem., 38 (1975) 385.
5 J.A. Ibers and B.L. Haymore, Inorg. Chem., 14 (1975) 1369.
6 G.N. Schrauzer, Chem. Ber., 94 (1961) 1841.
7 J.C. Clark and R.C. Cookson, J. Chem. Soc., (1962) 686.
8 B. Carroll and J.C. Lalore, J. Organomet. Chem., 37 (1973) 54.
9 R.M. Kluber and J.W. Lewis, J. Am. Chem. Soc., 82 (1968) 5777.
10 A.M. Talati and R.N. Kapadia, Indian J. Chem., 12 (1974) 767.
11 G. Rosini, J. Org. Chem., 39 (1974) 3504.
12 L.I. Bellamy, Infrared Spectra of Complex Molecules, Methuen, London, 1958.
13 K. Krishnakutty and P. Umar, J. Ind. Chem. Soc., 65 (1988) 213; J. Ind. Chem. Soc., 66 (1989) 194.
14 J. Selbin, Coord. Chem. Rev., 1 (1989) 194.
W.A. Baker and M.N. Bobonich, Inorg. Chem., 3 (1964) 1184.
F. Cotton and C. Wilkinson, Advanced Inorganic Chemistry, Wiley-Interscience, New York, 1961.
15 A. Deshmukh, Ph.D. Thesis, Bombay University, 1989.
A.Y. Desai and A.D. Sawant, Asian J. Chem., 5 (1993) 881.
16 E. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
17 B.D. Stepin, G.P. Allakhvedrov and G.M. Serebrennikova, Zh. Fiz. Khim., 43 (1969) 2452.
18 F.C. Chang and W.W. Wendlandt, Thermochim. Acta, 7 (1973) 103.