This article was downloaded by: [RMIT University] On: 26 June 2013, At: 19:26 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



Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsrt19

Synthesis and Thermal Studies on Some Bimetallic Mixed-Ligand Complexes Containing a Bis-Bidentate Onno Schiff Base and Alkylxanthate Ligands

Asma I. EI-Said ^a

^a Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt Published online: 23 Apr 2008.

To cite this article: Asma I. El-Said (1999): Synthesis and Thermal Studies on Some Bimetallic Mixed-Ligand Complexes Containing a Bis-Bidentate Onno Schiff Base and Alkylxanthate Ligands, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 29:8, 1411-1426

To link to this article: http://dx.doi.org/10.1080/00945719909351708

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <u>http://www.tandfonline.com/page/terms-and-conditions</u>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, 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.

SYNTHESIS AND THERMAL STUDIES ON SOME BIMETALLIC MIXED-LIGAND COMPLEXES CONTAINING A BIS-BIDENTATE ONNO SCHIFF BASE AND ALKYLXANTHATE LIGANDS

Asma I. El-Said

Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt.

ABSTRACT

New bimetallic mixed-ligand complexes of the general formula $[M_2(sal-bz)(Rxan)_2(DMF)_n]$, where M = Ni(II), Co(II) or Cu(II); sal-bz = dianion of a tetradentate Schiff base derived from salicylaldehyde and benzidine; xan = xanthate anion; R = methyl, ethyl or butyl; n = 2 or 4, have been prepared and characterized by elemental analyses, molar conductance, IR and electronic spectral data. The thermal decomposition of some of these complexes has been studied. The TG curves show that the decomposition takes place in two well-defined steps. The first step involves the elimination of DMF molecules and the decomposition of the alkyl xanthate via a radical mechanism. This was accompanied by the formation of an intermediate product which decomposed in a second step to the metal sulphide as the end product. Activation energies and other kinetic parameters were computed.

1411

INTRODUCTION

Schiff bases derived from the condensation of salicylaldehyde with alkyl- or arylamines, known as N-alkyl- or N-arylsalicylaldimines, are considered to be suitable models for pyridoxal and, in general, B_6 vitamines¹. The chemistry of metal complexes with quadridentate Schiff base ligands has been studied²⁻⁹ extensively. Furthermore, there has been increasing interest in the chemistry of transition metal complexes of xanthates for their industrial applications¹⁰. They have also been used as insecticides, fungicides and antioxidants^{11,12}.

To our knowledge, there are no reports dealing with mixed-ligand complexes containing bridged Schiff bases (derived from salicylaldehyde) and alkyl xanthates. Also, only a few thermal analysis studies of mixed-ligand xanthato complexes have been puplished^{13,14}. Therefore, and in connection with our previous studies on metal dithiolates,¹⁵⁻²⁰ we report herein the preparation of some mixed-ligand complexes formed between a bridged Schiff base (derived from the condensation of salicylaldehyde and benzidine) and methyl, ethyl or butyl xanthate (Fig. 1). The metal ions used are nickel(II), cobalt(II) and copper(II). Thermal studies have also been carried out on some of the prepared complexes.

RESULTS AND DISCUSSION

The chemical composition and some physical properties of the prepared compounds are given in Table I. The chemical data show 2:1:2 molar ratio reactions of the metal salts with the Schiff base and alkyl xanthates to produce complexes of the general formula $[M_2(sal-bz)(Rxan)_2(DMF)_n]$ where n = 2 or 4. The formation of the



Fig. 1. Structure of the Ligands

complexes may be represented by the following equation:

2 MCl₂ + sal-bzH₂ + 2 KRxan $\xrightarrow{n DMF}$ [M₂(sal-bz)(Rxan)₂(DMF)_n] + 2 KCl + 2 HCl

sal-bzH₂ = Schiff base derived from salicylaldehyde and benzidine; R = methyl, ethyl or butyl; n = 4 for M = Co(II) or Ni(II) and n = 2 for M = Cu(II).

The complexes are readily soluble in chloroform and to a lesser extent in acetone, methanol or ethanol. The molar conductivities are in the 2.3-9.8 Ω^{-1} cm² mol⁻¹ range, commensurate with non-electrolytic behaviour²¹.

IR Spectra

The infrared spectra of the complexes exhibit absorptions typical of a coordinated alkyl xanthate and Schiff base. The main IR spectral bands are recorded in Table II. For the Schiff base moiety, the band observed in the region 1615-1630 cm⁻¹ indicates the bonding of the azomethine nitrogen to the metal centers²². The coordination of the phenolic oxygen to the metal ions is manifested by the increase in the v(C-O) frequency (1210-1245 cm⁻¹)

R = butyl, Buxan

ne 2013
26 Ju
19:27
] at
niversity
RMIT U
by
Downloaded

Table I. Colour, Analytical Data, Yields, Melting Points and Molar Conductance of the Complexes.

<u> </u>		T							
Λ_{M}	ohm ⁻¹ cm ² mol ⁻¹	6.2	4.9	5.7	2.3	3.9	9.8	8.3	7.5
M.p.	S	110	125	125	190	195	200	210	208
Yield	%	56	87	75	83	85	66	73	81
	S	12.86 (12.64)	12.36 (12.30)	11.88 (11.67)	12.14 (12.30)	11.72 (11.67)	14.45 (14.61)	14.18 (14.15)	13.16 (13.33)
alc.), %	Z	8.45 (8.28)	8.08 (8.06)	7.57 (7.65)	7.98 (8.06)	7.53 (7.65)	6.57 (6.38)	6.21 (6.18)	5.57 (5.82)
Found (C	н	5.12 (5.17)	5.32 (5.41)	5.88 (5.87)	5.35 (5.41)	5.81 (5.87)	4.32 (4.36)	4.62 (4.67)	5.35 (5.24)
	C	49.59 (49.72)	50.52 (50.69)	52.39 (52.47)	50.96 (50.67)	52.27 (52.45)	49.11 (49.24)	50.40 (50.37)	52.60 (52.43)
	Colour	brownish- green	orange	yellowish- green	yellowish- green	dark green	brown	yellowish- green	yellowish- green
Compound	(Empirical formula) (Formula weight)		[Ni2(sal-bz)(Etxan)2(DMF)4] (Ni2C44H56N6O8S4) (1042.64)	[Ni2(sal-bz)(Buxan)2(DMF)4] (Ni2C48H64N6O8S4) (1098.75)	[Co ₂ (sal-bz)(Etxan) ₂ (DMF) ₄] (CO ₂ C ₄₄ H ₅₆ N ₆ O ₈ S ₄) (1043.09)	[Co ₂ (sal-bz)(Buxan) ₂ (DMF) ₄] (CO ₂ C ₄₈ H ₆₄ N ₆ O ₈ S ₄) (1099.20)	$\label{eq:constraint} \begin{split} & [Cu_2(sal-bz)(Mexan)_2(DMF)_2] \\ & (Cu_2C_{36}H_{38}N_4O_6S_4) \ (878.06) \end{split}$	$\label{eq:constraint} \begin{split} & [Cu_2(sal-bz)(Etxan)_2(DMF)_2] \\ & (Cu_2C_{38}H_{42}N_4O_6S_4) \ (906.11) \end{split}$	[Cu ₂ (sal-bz)(Buxan) ₂ (DMF) ₂] (Cu ₂ C ₄ 2H ₅₀ N ₄ O ₆ S ₄) (962.22)

Table II. Important IR Bands (cm⁻¹) and Electronic Spectral Data of the Complexes (cm⁻¹) (ϵ_{max} , M^{-1} cm⁻¹)

-		IR Spect	ra (cm ⁻¹)			Electronic !	Spectra (cm ⁻¹)	Intraligand
Compound	Schiff 14(C=O)	base (C=N)	Xant D(C=O)	hate v(C=S)	d-d	Charge transfer	Imine π-π* (Schiff base)	transition (Xanthate)
		6						
[Ni ₂ (sal-bz)(Mexan) ₂ (DMF) ₄]	1230 s	1615 m	1140 m	1040 s	15.873 (625)	20 833 (1016)	27.174 (31333)	32.258 (34533)
[Ni2(sal-bz)(Etxan)2(DMF),]	1245 s	1620 m	1140 m	1020 s	15 504 (187)	20.883 (2377)	27 027 (32000)	31 746 (62742)
[Ni ₂ (sal-bz)(Buxan) ₂ (DMF) ₄]	1220 m	1620 w	1125 m	1020 m	15 625 (150)	20 833 (1050)	27.174 (32323)	31.746 (36342)
[Co ₂ (sal-bz)(Etxan) ₂ (DMF) ₄]	1245 \$	1620 w	1120 s	1030 s	16 129 (136)	20 833 (2321)	27 027 (27272)	35 087 (11333)
[Co ₂ (sal-bz)(Buxan) ₂ (DMF) ₄]	1240 w	1620 w	l125 m	1040 s	16.000 (148)	20 619 (2506)	27.174 (23615)	36.364 (21514)
[Cu ₂ (sal-bz)(Mexan) ₂ (DMF) ₄]	1210 w	1630 m	1130 w	1030 m	13.986 (84)	21 739 (2412)	27 548 (37795)	35 714 (11435)
$[Cu_2(sal-bz)(Etxan)_2(DMF)_4]$	12i0 s	1620 m	1120 s	1030 s	13 889 (112)	21 277 (2076)	27.174 (35504)	35 714 (22047)
[Cu ₂ (sal-bz)(Buxan) ₂ (DMF) ₄]	1210 s	1610 m	1120 s	1040 s	13.928 (118)	21 053 (1814)	27.027 (11624)	35 714 (10323)

Key's (strong), m (medium), w (weak).

as compared with that of the free ligand^{23,24} (1195 cm⁻¹). The formation of dinuclear complexes may be attributed to the <u>para-position</u> of the azomethine nitrogen in the Schiff base (sal-bzH₂), wherein coordination of both azomethine nitrogens to the same metal ion is difficult. Thus, the Schiff base behaves as a bis-bidentate ligand coordinating to the metal ions through the imine nitrogen and the phenolic oxygen atoms.

The bands in the regions 1120-1140 cm⁻¹ and 1020-1040 cm⁻¹ are tentatively assigned to υ (C-O) and υ (C=S) of alkyl xanthates, respectively^{25,26} The location of the latter band in all complexes may be considered as a confirmation of the bidentate nature of the xanthate group since it appears as a single band in that region²⁷. In all compounds the additional characteristic band observed in the region 1640-1670 cm⁻¹ is assignable to υ (C=O) of coordinated DMF⁹.

Electronic Spectra

The electronic spectral data of the complexes are recorded in Table II. The spectra of the complexes were measured in chloroform solution. The spectra of the Ni(II) complexes display a d-d band in the region 15,504-15,873 cm⁻¹ (${}^{3}T_{1g} \leftarrow {}^{3}A_{2g}$). The appearance of this band is typical of octahedrally coordinated Ni(II). For the Co(II) complexes the band at 16,000-16,129 cm⁻¹ is ascribed to the d-d transition ${}^{4}T_{1g}(P) \leftarrow {}^{4}T_{1g}$ characteristic of octahedral Co(II) complexes. Additional d-d transitions are obscured by the charge transfer band. The Cu(II) complexes exhibit the d-d transitions at 13,889-13,986 cm⁻¹ which are similar to that of penta-coordinate Schiff base complexes of Cu(II)²⁸. Thus, a square-pyramidal arrangement may be suggested for these complexes.

On the basis of their high intensity ($\varepsilon = 1016-2506 \text{ M}^{-1}\text{cm}^{-1}$), bands occuring in the region 20,619-21,739 cm⁻¹ for all complexes are ascribed to charge transfer transitions, most probably L \rightarrow M. The absorption bands, which are located in the region 27,027-27,548 cm⁻¹ may be assigned to the imine $\pi - \pi^*$ transition of the Schiff base ligand¹. Further, the bands appearing at 31,746-36,364 cm⁻¹ evidently are internal transitions in the alkyl xanthate moiety²⁹.

The suggested structural formulation of the complexes may be represented as follows in Fig. 2.

Thermal Behaviour

The thermal decomposition of some of the prepared complexes was studied in the temperature range from ambient up to 550° C in static air. The complexes are $[Ni_2(sal-bz)(Etxan)_2(DMF)_4]$, $[Ni_2(sal-bz)(Buxan)_2(DMF)_4]$, $[Co_2(sal-bz)(Buxan)_2(DMF)_4]$, $[Co_2(sal-bz)(Etxan)_2(DMF)_2]$ and $[Cu_2(sal-bz)(Buxan)_2(DMF)_2]$. A computer program³⁰ which enables regression analysis and determination of kinetic and thermodynamic parameters from experimental TG/DTG non-isothermal thermogravimetric data has been used. This program allows the Coats-Redfern and Horowitz-Metzger methods^{31,32} to be performed for up to 14 different solid-state rate-controlling reactions, including *n*th-order Avrami-Erofeev³³ phase boundary movement and diffusional models. The results are summarized in Table III.

The TG curves of the compounds exhibit two distinct steps in the temperature ranges 180-220° C and 370-485° C, respectively. In the first step, the xanthate moiety is undergoing decomposition, while the Schiff



base part remained intact. It was proposed that the decomposition of the alkyl xanthate moiety proceeds via a radical mechanism $[2RO(S) \notin S \rightarrow 2S + 2RO-\dot{C}(S)]$ with the formation of a thermally stable intermediate product (Fig. 3): this was accompanied by the loss of DMF molecules and a volatile decomposition product (RO-C(S)-C(S)-OR) The stability of the intermediates is achieved from the TG curves, since the plateaus corresponding to the first step extend over a temperature range of about 150-165° C, beyond which the second step sets in The observed weight loss for this step (30.94-39.13%) is in good agreement with the theoretical values (31.11-39.55%), for the studied complexes.

To obtain intermediates, the initial complexes were non-isothermally heated up to the temperature corresponding to the end of the first Downloaded by [RMIT University] at 19:27 26 June 2013

log A (s-1) 17 34 9 13 28 17 9 5 9 5 I3 7 Kinetic Model (KM) Fn 1 Fn 2 Fn 2 Fn 2 Fn 2 Fn 2 Fn l Fn 0 Fn 0 Fn 2 Fn 2 2 Fn 0 Fn 0 Fn 2 Fn 2 Fn $(J mol^{-1}K^{-1})$ ∆S* -30 -- 66 -33 -23 -60 -15 -62 -28 -50 -67 -34 . $(kJ mol^{-1})$ *H⊅ 303 139 161 248 260 210 220 307 115 99 142 159 29 140 135 150 (kJ mol⁻¹) 145 167 252 264 158 172 119 148 165 **ж** 307 311 103 133 144 |41 |56 Horowitz-Metzeger Iorowitz-Metzeger Horowitz-Metzeger **Horowitz-Metzeger** Horowitz-Metzger Horowitz-Metzger Horowitz-Metzger Horowitz-Metzger Coats-Redfern Coats-Redfern Coats-Redfern Coats-Redfern Coats-Redfern Coats-Redfern Coats-Redfern Coats-Redfern Method Dec. temp. () () 485 185 445 200 475 195 440 220 Step 2 2 2 ----2 $[Ni_2(sal-bz)(Butxan)_2(DMF)_4]$ Co₂(sal-bz)(Butxan)₂(DMF)₄] $[Co_2(sal-bz)(Etxan)_2(DMF)_4]$ $[Ni_2(sal-bz)(Etxan)_2(DMF)_4]$ Compound

Table III. Decomposition Temperatures and Computed Kinetic Parameters for the Complexes.

(continued)

3
01
6
June
26.
9:27
at 1
2
ersity
jiv
Б
ШŢ
\mathbb{R}
by
g
ade
llo
IWC
Ă

Table III. Continued.

	c	Dec.	-	Е*	ΔH*	ΔS^*	Kinetic	log A (
Compound	Step	(°C).	Wethod	(kJ mol ⁻¹)	(kJ mol ⁻¹)	$(J \text{ mol}^{-1} K^{-1})$	Model (KM)	(s ⁻¹)
sal-bz)(Etxan)2(DMF)2]		180	Coats-Redfern	179	175	-26	Fn 2	10
			Horowitz-Metzeger	182	178	ı	Fn 2	19
	7	370	Coats-Redfern	109	104	-70	Fn 2	5
			Horowitz-Metzger	125	119	-44	Fn 2	8
sal-bz)(Buxan)2(DMF)2	1	195	Coats-Redfern	158	119	-53	Fn 2	6
			Horowitz-Metzeger	173	169	t	Fn 2	17
	C1	380	Coats-Redfern	84	115	-78	Fn 2	m
			Horowitz-Metzger	103	97	12-	Fn 2	S



M = Ni(II) or Co(II); R = ethyl or butyl

Fig. 3. Proposed Mechanism of the First Decomposition Step.

decomposition step. The composition assigned to the intermediates on the weight loss basis was further confirmed by IR spectral studies. The spectra of the intermediates reveal the presence of the coordinated Schiff base, as determined by the fact that the characteristic bands of the Schiff base are located at the same positions as for the initial complexes (Table II). Also, the appearance of a new band in the range 450-460 cm⁻¹, typical for S-S bond³⁴ supports the proposed structure of the intermediates.

In the case of the Cu(II) complexes, the intermediate may be stabilized by molecular association (Fig. 4).



Fig. 4. Suggested Structure of the Cu(II) intermediate.

The non-isothermal-kinetics of the two decomposition steps of the complexes is listed in Table III. It can be concluded that the activation energies for the first decomposition step vary greatly among the complexes indicating different thermal stabilities. The following thermal stability order can be recognized:

$$Co(II) \le Cu(II) \le Ni(II)$$

This behaviour may be attributed to the variable degree of the ionic character in the metal-sulphur, metal-nitrogen, or metal-oxygen bonds in the complexes³⁵. The lower stability of the cobalt(II) complexes might be attributed to the autocatalytic effect of the cobalt(II) ion. Additional intermolecular factors may operate and control the stability of the complexes.

It is obvious from the results obtained that different kinetic models³³ govern the first step in the decomposition process for the various complexes. The complexes $[Ni_2(sal-bz)(Etxan)_2(DMF)_4],$ $[Cu_2(sal-bz)(Etxan)_2(DMF)_2]$ and $[Cu_2(sal-bz)(Buxan)_2(DMF)_2]$ are governed by phase-boundary movement (Fn 2); one-dimensional movement of the phase-boundary (Fn 0) is the rate controlling mechanism for $[Co_2(sal-bz)(Etxan)_2(DMF)_4]$ and $[Co_2(sal-bz)(Buxan)_2(DMF)_4]$ while random nucleation (Fn 1) governed the first decomposition step of the complex $[Ni_2(sal-bz)(Buxan)_2(DMF)_4]$. Fn 2, Fn 0 and Fn 1 correspond^{30,33} to the $g(\alpha)$ functions $[1-(1-\alpha)^{1-n}] / (1-n), \alpha$, $-\ln(1-\alpha)$ respectively, which give the best fit of data; α is the fraction decomposed and *n* is the reaction order.

In all the complexes studied the second step represents the decomposition of the intermediates formed in the first step with the formation of metal sulphide as the end product. Sulphur analysis and the observed overall weight loss range (83.09-78.58%) versus the calculated values (83.48-78.90%) are in agreement with the formation of metal sulphides^{13,17}. The relatively low values of activation energies of the copper(II) intermediates suggest that the bonding is weaker in the copper(II) intermediates than in the cobalt(II) and nickel(II) intermediates.

The activation enthalpies (ΔH^*) have the same trends as the activation energies. The negative values of the activation entropies (ΔS^*) in these complexes indicate that the activated complex has a more ordered structure than the reactants and that the reactions are slower than normal³⁶.

EXPERIMENTAL

All chemicals were of analytical grade. The Schiff base ligand was prepared by the usual condensation method⁹. Potassium alkyl xanthates were prepared according to previously published methods¹⁰. The IR spectra of the complexes were recorded on a Shimadzu IR-470 spectrophotometer and electronic spectra were obtained using a Shimadzu UV-2101 PC spectrophotometer. Conductivity measurements were made using a LF Digi

550 conductance bridge. Thermal studies were carried out as described previonsly¹⁷ with the aid of a Sartorius 2003 MP electrobalance converted to a thermobalance by the addition of a small furnace and sample holder. The temperature was measured using a chromal-alumal thermocouple attached to a type Soor MF 550 digital multimeter, the heating rate was adjusted to 7° C min⁻¹.

Preparation of the Complexes

Since the preparation of the complexes followed essentially similar procedures, a general method will be described. To 20 mL of a hot dimethylformamide solution of the Schiff base salicylaldehyde-benzidine (0.2 g, 0.5 mmol), a solution of the metal chloride (1 mmol) in 10 mL methanol was added with constant stirring. To the above mixture, 10 mL of an aqueous solution of potassium alkyl xanthate (1 mmol) was added with constant stirring. The complexes were precipitated by addition of distilled water. The products were filtered, washed with a little dimethylformamide (5 mL) and dried over P_4O_{10} .

REFERENCES

- A. S. N. Murthy and A. R. Reddy, Proc. Indian Acad. Sci. (Chem. Sci.), <u>90</u>, 519 (1981).
- G. Costa, G. Mestroni, G. Tauzher and L. Stefani, J. Organometal. Chem., <u>6</u>, 181 (1966).
- M. H. Darbieu, G. Cros, D. Montauzon and J. Laurent, Transition Metal Chem., <u>7</u>, 149 (1982).
- 4. Y. Nishida and S. Kida, Inorg. Chim. Acta, <u>49</u>, 85 (1981).

- E. F. Hasty, L. J. Wilson and D. N. Hendrikson, Inorg. Chem., <u>17</u>, 1834 (1978).
- 6. P. Cassoux and A. Gleizes, Inorg. Chem., <u>19</u>, 665 (1980).
- B. B. Mahapatra and S. C. Chaudhury, Ind. J. of Chem., <u>28</u>A, 533 (1989).
- A. M. A. Hassaan, Synth. React. Inorg. Met. Org.-Chem., <u>27</u>, 921 (1997).
- N. S. Rao, D. D. Mishra and R. C. Maurya, Synth. React. Inorg. Met.-Org. Chem., <u>25</u>, 437 (1995).
- S. R. Rao, "Xanthates and Related Compounds", Marcel Dekker, New York, (1971).
- G. J. M. Van der Kerk and H. L. Klopping, Rec. Trav. Chim. Pays-Bas, <u>71</u>, 1179 (1952); Nature (London) <u>176</u>, 308 (1955).
- 12. D. Coucouvanis, Prog. Inorg. Chem., <u>11</u>, 233 (1970).
- 13. J. O. Hill and R. J. Maggee, Rev. Inorg. Chem., <u>3</u>, 141 (1981).
- J. O. Hill, J. P. Murray and K. C. Patil, Rev. Inorg. Chem., <u>14</u>, 363 (1994).
- 15. A. A. M. Aly and A. I. El-Said, Z. Naturforsch., <u>44</u>b, 323 (1989).
- A. I. El-Said and A. A. M. Aly, Synth. React. Inorg. Met.-Org. Chem., <u>20</u>, 1059 (1990).
- 17. A. I. El-Said, Transition Met. Chem., <u>17</u>, 130 (1992).
- A. S. A. Zidan, A. I. El-Said and A. A. M. Aly, Synth. React. Inorg. Met. Org. Chem., <u>22</u>, 1355 (1992).
- A. A. M. Aly, M. M. Kamal, M. S. El Meligy and A. I. El-Said, Z. Naturforsch., <u>39</u>b, 1676 (1984).

- A. A. M. Aly, M. M. Kamal, M. S. El Meligy and A. I. El-Said, Z. Naturforsch., <u>42</u>b, 233 (1987).
- 21. W. J. Geary, Coord. Chem. Rev., 7, 81 (1971).
- 22. S. Yamada, Coord. Chem. Rev., <u>1</u>, 415 (1966).
- R. C. Maurya, D. D. Mishra, N. S. Rao and N. N. Rao, Polyhedron, <u>22</u>, 2837 (1992).
- 24. C. Natarajan and P. Tharmaraj, Indian J. Chem., <u>30A</u>, 722 (1991).
- R. N. Murty, R. A. Dash and D. V. R. Rao, J. Ind. Chem. Soc., <u>LXI</u>, 943 (1984).
- 26. A. G. Krüger and G. Winter, Aust. J. Chem., 24, 161 (1971).
- 27. F. Bonati and R. Ugo, J. Organomet. Chem., <u>10</u>, 257 (1967).
- 28. R. H. Balundgi and A. Chakravorty, Inorg. Chem., 12, 981 (1973).
- 29. C. K. Jørgensen, J. Inorg. Nucl. Chem., <u>24</u>, 1571 (1962).
- 30. M. A. A. Beg and M. A. Qaiser, Thermochim. Acta, <u>173</u>, 281 (1990).
- 31. A.W. Coats and J.P. Redfern, Nature, <u>20</u>, 68 (1964).
- 32. H.H. Horowitz and G. Metzger, Anal. Chem., <u>35</u>, 1464 (1963).
- 33. A. M. M. Gadalla, Thermochim. Acta, <u>74</u>, 255 (1984).
- J. B. Lambert, H. F. Shurvell, L. Verbit, R. G. Cooks and G. H. Staut, "Organic Structural Analysis", Macmillan, New York (1976).
- 35. M. Tomassetti, E. Cardarelli, R. Curini and G. D. Ascenzo, Thermochim. Acta, <u>113</u>, 243 (1987).
- A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", John Wiley, New York (1961).

Received:	10 September 1998	Referee I:	S. E . Lincoln
Accepted:	13 May 1999	Referee II:	D. E. Pennington