THERMAL STUDIES ON ADDITION COMPOUNDS OF BIS(ETHYLXANTHATO)NICKEL(II)

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ABSTRACT

Ni(xanthate)$_2$, a diamagnetic square planar complex forms $1:1$ six-coordinated high-spin paramagnetic adducts with dinitrogen donors in different organic solvents. The thermal studies of these compounds show the loss of trapped solvent (ether) followed by the loss of the addendum leaving behind the parent xanthate complex. In the compounds with $1:3$ ratio of Ni(xanthate):dinitrogen donors, the xan$^-$ acts as an anion. The different steps of thermal decomposition in the compounds, Ni(phen)$_3$xan$_2$ and Ni(bipy)$_3$xan$_2$, can be explained on the basis of the conformational rigidity of the ligands. For the parent compound Ni(xan)$_2$, its $1:1$ and $1:3$ adducts as well as the thermal decomposition products (residues) have been analysed by chemical and physical methods. New intermediate complexes with the composition, Ni(phen)$_2$xan$_2$, Ni(bipy)S$_2$ and Ni(bipy)S have been obtained from the decomposition process, leading finally to NiO. The kinetic parameters were calculated using five different methods to check the applicability of these standard methods towards the elucidation of the decomposition mechanism.

INTRODUCTION

The compound bis(ethylxanthato)nickel(II), Ni(xan)$_2$, is a diamagnetic, low-spin complex with square planar coordination around the nickel [1–3]. Availability of the axial dz^2 electron pair on the nickel orbitals assists the formation of a five- or six-coordinated adduct with different donors yielding a coordinatively saturated high-spin paramagnetic compound. Three dinitrogen (N–N) donors, 1,10-phenanthroline (phen), 2,2'-bipyridyl (bipy), and ethylenediamine (en), form both $1:1$ and $1:3$ adducts which are reported by Krüger and Winter [4]. These are known to form inclusion compounds with solvents in which they are prepared. In the present communication it is intended to present the kinetic and mechanistic study, using dynamic thermal methods, for these adducts. Thermal decompositional studies on Ni(xan)$_2$ reported [5] from this laboratory showed the formation of NiS and mostly stoichiometric NiO.

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EXPERIMENTAL

All the reagents used were Analar grade unless otherwise stated and were used without further purification.

Synthesis

(a) Bis(ethylxanthato)nickel(II) was prepared as reported in the literature [4].

(b) Mono-N–N-nickel(II)-bisethylxanthate: Ni(xan)$_2$ and the corresponding di-nitrogen donor, N–N [phen, bipy, *o*-diaminobenzene (dab)], in 1:1 mole ratio were treated in diethyl ether or carbon tetrachloride and stirred for two hours to yield the crystalline products.

(c) Tris-N–N-nickel(II)-bisethylxanthate: A little in excess of a 1:3 mole ratio of Ni(xan)$_2$: N–N, was dissolved in acetone and refluxed for one hour to yield a shiny yellow crystalline product with phen and bipy and a pink coloured product with en; dab yielded some decomposed material which was, therefore, not characterized.

Physico-chemical studies

The mono and tris adducts were analysed for the elements in the microanalytical laboratory in the authors' department. The adducts were further characterized using solution conductivity, magnetic susceptibility, infrared spectra and electronic spectra.

Thermogravimetric (TG/DTG/DTA) analysis was carried out on MOM deriva-tograph at a heating rate of 3°C min^{-1}, in a platinum crucible in air.

Calculations

The data from TG/DTG/DTA were processed for the kinetic parameters E_a, K, and n using mechanism-non-invoking [6–10] and mechanism-invoking [11,12] relations. The shape of the DTA/DTG curve was assumed to be of a Gaussian type and the standard equation of Gaussian curve analysis [6] was employed for the resolution of the overlapping envelopes needed to calculate areas. A computer program CAL was developed by the authors [5] to use on an ICL-1904S computer at the University of Poona, for the calculation of various kinetic parameters. It is based on the least squares fitting of the kinetic parameters and provides, in a single run, the kinetic parameter calculations by different methods. The program has a built-in optional facility of plotting Satava [11] type [log g(α) against 1/T] graphs. The program needs 50 s to process the results for the data of one compound through mechanism-invoking and mechanism-non-invoking relations including plotting.

The assignments of the spectral transitions were based on the curve-fitting program SPECTRA developed by the authors [13] using standard procedures [14].

RESULTS AND DISCUSSION

The formation of 1:1 adducts of phen, bipy, and en with $Ni(xan)_2$ have been reported previously [4]; however, the 1:1 adduct of dab is reported for the first time. The isolation of the 1:3 adduct of dab was not possible. Table 1 presents the data on elemental analysis and general physical properties of these adducts. Table 1 reveals that the parent complex, $Ni(xan)_2$ and its 1:1 adducts are non-electrolytic in solution while the tris adducts are 1:2 electrolytes in solution. It shows undoubtedly that the xanthato groups from the parent bis chelate have been displaced from square plane and act as anions in their tris-(N–N) adducts. The infrared absorption bands characteristic of a coordinated xanthato group at 1270 cm^{-1}, due to C–O–C and at 1030 cm^{-1} due to C=S showed a low frequency shift of about 65–85 cm^{-1} in the 1:1 adducts and a shift of 70–100 cm^{-1} in 1:3 adducts. This low frequency shift was attributed to the removal of electron delocalization in C–O–C and C=S bonds of the free xanthate anion.

The electronic spectral absorptions of 1:1 adducts with phen, bipy and en are given in the literature and are confirmed in the present work (Table 1); the 1:1 adduct of dab does not differ much from the above trend. The spectral assignments for the 1:3 adduct with phen match well with the reported data [15]. Spectral calculations showed that the 1:1 and 1:3 adducts exhibit an octahedral configuration. This is also supported from the magnetic moments which fall between 3.01 and 3.20 B.M. (Table 1).

Table 2 presents the TG data for different compounds and contains the temperature range for decomposition, percent loss and probable composition of the expelled groups and the residues. The discussion may be conveniently split into three groups.

(1) The parent xanthate complex. It is reported [16] that the chain length of R in the R–O–CSS$^-$ has a pronounced effect on the thermal stability of the xanthates. The decomposition temperatures of Ni(methyl xanthate)$_2$, Ni(propyl xanthate)$_2$, and Ni(i-propyl xanthate)$_2$ were respectively 240, 163 and 235°C [13]. In this paper, however, the studies on Ni(ethyl xanthate)$_2$ and its adducts are discussed.

As reported [5] $Ni(xan)_2$ yielded NiS in the first major step of decomposition which then further lost sulphur to yield NiO.

(2) Mono adducts of N–N donors. The mono adducts of $Ni(xan)_2$ with phen, bipy and dab have the tendency to trap solvent molecules in their lattices during the process of crystallization. The TG losses in the present work supported this finding. The DTG and DTA curves clearly showed the presence of two loss processes overlapping each other (Fig. 1). The losses could be quite satisfactorily fitted to the loss of one solvent molecule and one ligand per complex molecule (Table 2). The trapped solvent, ether, is lost earlier.

The second characteristic of all the mono adducts is the loss of the addendum leaving behind $Ni(xan)_2$. The characterization of the residues has been done by studying the infrared spectra which were found to be identical with the parent xanthato complex. The low temperatures (Table 2) required for the expulsion of the addendum shows the weakness of the bonding between nickel and N–N. The

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TABLE 1

Elemental analysis and general physical properties

No.	Compound [a]	Analysis % Ni (calcd.)	% S (calcd.)	Colour	Conductance [b] (Ω^{-1} mole^{-1} cm^2)	Magnetic moment (B.M.)	Band position [c] (cm^{-1})
1	Ni(xan)$_2$	19.4 (19.51)	41.9 (42.62)	Dark red	2.0	Diamagnetic	15750, 20830, 23830
2	Ni(xan)$_2$·phen ether	10.7 (10.59)	23.6 (23.10)	Green	8.0	3.04	10400, 16310, 25900
3	Ni(xan)$_2$·bipy ether	10.9 (11.07)	24.0 (24.15)	Green	7.0	3.03	10420, 16350, 25975
4	Ni(xan)$_2$·dab ether	11.9 (12.20)	26.4 (26.61)	Dark green	3.0	3.01	10420, 16340, 25985
5	Ni(xan)$_2$·en ether	13.3 (13.52)	29.1 (29.49)	Green	6.0	3.04	10440, 16600, 26110
6	Ni(phen)$_3$xan$_2$	7.0 (6.98)	15.4 (15.22)	Yellow	134.0	3.12	12315, 18325, 28485
7	Ni(bipy)$_3$xan$_2$	7.39 (7.63)	16.2 (16.65)	Yellow	129.0	3.11	11900, 17600, 27350
8	Ni(en)$_3$xan$_2$	12.1 (12.21)	26.8 (26.62)	Pink-violet	140.0	3.19	11100, 17605, 28280

[a] Analysis of carbon, hydrogen and nitrogen carried out in the microanalytical laboratory, Department of Chemistry, University of Poona, were found to agree with the empirical formulae.
[b] Philips GM 4144 bridge; solvent DMF.
[c] Beckman DK2 ratio recording spectrophotometer; solvent ethyl alcohol.

TABLE 2

Thermogravimetric data on parent complex and adducts

No.	Compound	Temp. range of decomposition (°C)	% loss (calcd.)	Probable composition of expelled group [a]	Composition of residue
1	$Ni(xan)_2$	180–240	69.8 (70.0)	Cos. SC $\begin{matrix} SR \\ OR \end{matrix}$	NiS
		600–615	5.1 (5.3)	SO_2	NiO
2	$Ni(xan)_2 \cdot$ phen ether	160–228	36.77 (37.0)	Ether, Phen	$Ni(xan)_2$
3	$Ni(xan)_2 \cdot$ bipy ether	126–136	14.0 (13.31)	Ether	$Ni(xan_2 \cdot bipy$
		136–185	30.0 (29.4)	bipy	$Ni(xan)_2$
4	$Ni(xan)_2 \cdot$ dab ether	110–150	38.0 (37.62)	Ether, dab	$Ni(xan)_2$
5	$Ni(xan)_2 \cdot$ en ether	100–140	31.2 (30.87)	Ether, en	$Ni(xan)_2$
6	$Ni(phen)_3 xan_2$	165–185	21.33 (21.41)	Phen	$Ni(phen)_2 xan_2$
		275–325	15.0 (14.34)	xan [a]	$Ni(phen)_2 xan$
7	$Ni(bipy)_3 xan_2$	85–260	64.0 (64.9)	2 bipy, sulphur [a] compounds	$Ni(bipy)S_2$
		322–353	4.4 (4.1)	SO_2	$Ni(bipy)S$
8	$Ni(en)_3 xan_2$	80–200	35.0 (34.88)	zen	$Ni(xan)_2$
		240–340	24.2 (23.25)	Sulphur [a] compounds	$Ni(xan)S$

[a] Many fragments from xan⁻ have been characterized by GC/MS (ref. 16).

examination of the DTA curves for mono adducts clearly shows an exothermic peak for the structural change just before the commencement of the decomposition. Thus the possible rearrangement of the molecular configuration that facilitates the expulsion of the N–N may be represented as shown in Fig. 2.

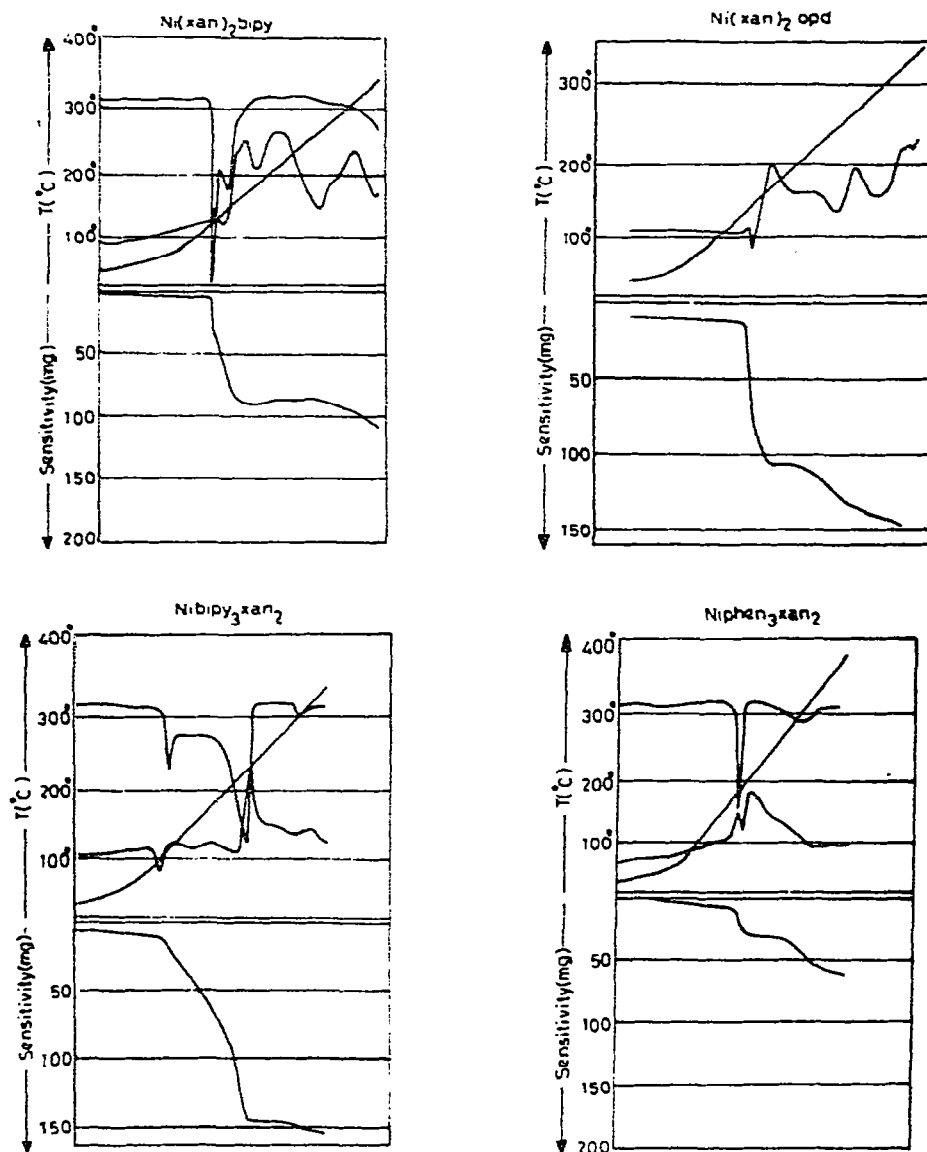(3) Tris-(N–N) adducts. The TG loss curve of $Ni(en)_3 xan_2$ fits with the two

Fig. I. The TG/DTA curves for the adducts.

step-losses as of three en molecules followed by one xan$^-$. This observation is, again, consistent with the TG losses of the mono-adducts, which shows that the addendum is lost first and the xan later.

The TG curve of Ni(phen)$_3$xan$_2$ shows a two-step loss. The first loss step is again due to one molecule of phen giving an intermediate complex Ni(phen)$_2$xan$_2$. This compound has been characterizaed by physical methods, like electronic and infrared spectra. The second loss starts at about 275°C, where one xan$^-$ is lost, leaving behind the composition Ni(phen)$_2$xan. However, this composition is not stable and readily starts decomposing further, leading to the formation of NiO at the end. On the other hand, the compound with bipy, Ni(bipy)$_3$xan$_2$, showed different thermal
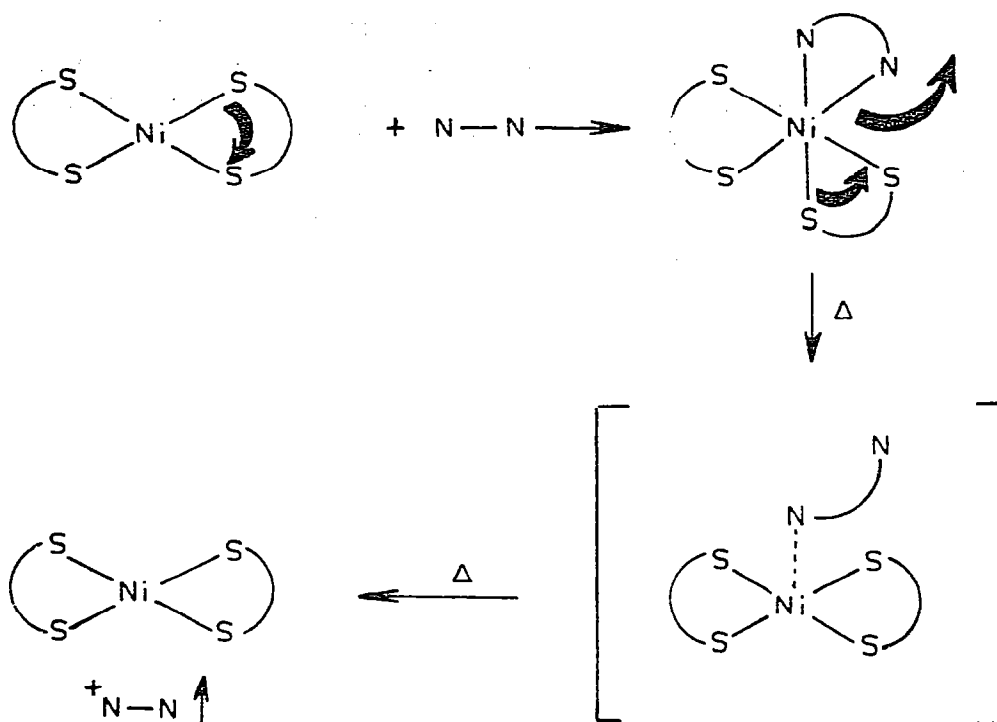
Fig. 2. Mechanism of loss of N–N (schematic).

behaviour. This fitted with the first heavy loss of two molecules of bipy and xanthates, leaving behind a residue with the composition Ni(bipy)S_2 at a temperature of 260°C. It is followed by a slow loss of one sulphur over the temperature range 322 to 353°C, forming Ni(bipy)S.

One interesting characteristic in the DTA curve of all these adducts is the presence of an exothermic peak for the weight loss processes. This may suggest that these tris adducts may be thermodynamically less stable than the subsequent decomposition products.

The difference in the behaviour of phen and bipy complexes is difficult to explain satisfactorily on the basis of thermal behaviour alone. One of the reasons could be the freedom of rotation in bipy about the 2-2′ bond. The configuration in phen is comparatively rigid. The flexibility of the 2-2′ bond in bipy is reported in the literature to be responsible for the increased rates of racemization in its complexes compared with that in the phen complexes [17]. Similarly, the overall formation constant for the phen complex of Ni(II) is about three orders of magnitude higher than that for the bipy complexes [17]. This increased stability parallels the higher thermal stability of ni(phen)$_3$xan$_2$ over that of Ni(bipy)$_3$xan$_2$; starting temperature for the thermal decomposition of Ni(phen)$_3$xan$_2$ is 165°C, whereas it is 85°C for Ni(bipy)$_3$xan$_2$.

The other interesting feature of these 1:1 and 1:3 adducts is the increased thermal stability of the xan⁻ group in comparison with that in the parent complex,

Ni(xan)$_2$. The complex Ni(ethyl xanthate)$_2$ starts decomposing at 180°C [5], while its mono and tris adducts lose the xanthate only above 200°C. It is, however, a general observation from the authors' laboratory that the parent complexes in their adducts show increased thermal stability [13,18–20]. Qualitatively, this phenomenon may be attributed to lattice stabilization effects.

The study of kinetic parameters computed from five different methods [6–11], can also be conveniently discussed in three parts.

(1) The parent complex. The details of thermal decomposition are reported [5] earlier. The activation energy calculation for the first step was done by two methods [6,10], using the data on DTG and they agree quite satisfactorily (240 kJ mole^{-1}) but were found to be somewhat higher than that obtained from the TG traces (Freeman and Carroll; 134.6 kJ mole^{-1}) (Table 3). However, the order of reaction by the former method is nearing unity while that by the latter is 0.5. The activation energy obtained from DTA is close to that from the DTG data (230 kJ mole^{-1}).

The second step due to the loss of sulphur is so small that within the accuracy of the measurements, a sufficient number of points from the curve could not be obtained to derive meaningful results.

(2) Mono adducts with N–N donors. The solvent loss step was discernible only in the adduct with bipy for which the activation energy is 159 kJ mole^{-1} (Freeman and Carroll) and 171 kJ mole^{-1} (Horowitz and Metzger). The other methods based on DTG and DTA showed lower E_a values except with the Arrhenius method (218 kJ mole^{-1}). It is interesting to note such a high value of E_a for ether compared with that for coordinated water [21]. If the solvent ether is considered to be lattice interacted then this value is lower than that for water [21], which is feasible on the basis of their configurations.

The second loss step is the loss of (N–N). The values in kJ mole^{-1} are in the order phen > bipy > dab. Further decomposition was a continuous loss leading finally to nickel oxide, similar to the loss curve of the parent complex. The lower magnitudes of rate constants for the expulsion of bipy compared with those for dab appears to be consistent with the higher ligand field of bipy. The low energy of activation for phen can also be explained on the basis of the rigidity of phen compared with the other ligand molecule.

(3) Tris (N–N) adducts. The decomposition of Ni(bipy)$_3$xan$_2$ shows a loss of about 68% which could be resolved into two components which correspond to activation energies of 84.9 and 58.9 kJ mole^{-1} (Freeman and Carroll), respectively. However, the complexity of the reaction prohibits the accurate characterization of the expelled group. The residue was analysed as Ni(bipy)S$_2$. A high activation energy (474 kJ mole^{-1}) for a DTA peak, corresponding to the structural change prior to the decomposition, permits one to assume dissociation and/or rearrangements of Ni–N bonds from the adduct. The E_a from the envelope in the DTA curve that represents compositional change is appreciably low (211 kJ mole^{-1}). The variation in the values of E_a's from TG and DTG methods is 15%, a value which is usually reported.

The other compound Ni(phen)$_3$xan$_2$ shows a loss of phen alone in the first step and a loss of one xan moiety in the second step. The activation energy for the first

TABLE 3

Data on activation energy and order of reaction

No.	Compound	Step	TG						DTG			DTA		
			FC [a]		CR [b]		HM [c]		Arrhenius		BD [d]	Arrhenius		BD [d]
			n	E_a (kJ mole^{-1})	n	E_a (kJ mole^{-1})	E_a (kJ mole^{-1})		n	E_a (kJ mole^{-1})	E_a (kJ mole^{-1})	n	E_a (kJ mole^{-1})	E_a (kJ mole^{-1})
1	Ni(xan)$_2$		0.43	134.6	1.0	171.2	141.0		1.03	248.0	240.7	0.87	183.1	283.8
2	Ni(xan)$_2$·phen ether		1.03	134.0	0.95	128.0	157.0		1.08	157.0	140.0			
3	Ni(xan)$_2$·bipy ether	I	0.31	159.0	0.7	165.0	171.0		0.80	87.0	104.0	1.66	218.0	151.0
		II	2.65	164.0	1.0	160.1	99.0		0.82	115.0	130.0	0.80	65.0	76.0
4	Ni(xan)$_2$·dab ether	I	1.21	176.0	1.0	189.7	182.0					1.16	114.8	101.7
		II	0.70	80.2	0.70	80.6	80.6					1.25	199.0	159.0
5	Ni(xan)$_2$·en ether		1.1	184.0	1.0	188.0	176.0		0.85	165.0	195.0	1.25	195.0	155.0
6	Ni(phen)$_3$xan$_2$	I	0.93	213.0	0.6	211.2	219.0		1.45	313.0	209.0	0.70	309.0	209.0
		II	1.51	114.0	0.75	118.0	108.0		1.32	156.0	126.0	1.37	223.0	163.0
7	Ni(bipy)$_3$xan$_2$	I	0.87	84.9	1.0	160.1	175.0					1.64	474.0	281.0
		II	1.89	58.9	1.0	42.2	36.2		0.18	72.0	109.0	1.77	211.0	97.3
8	Ni(en)$_3$xan$_2$	I	1.01	94.3	0.9	100.1	99.3		1.20	109.0	90.0	1.4	145.0	101.2
		II	1.75	139.3	1.0	156.2	141.2		0.8	135.0	160.5	1.3	181.0	140.1

[a] FC = Freeman and Carroll.
[b] CR = Coats and Redfern.
[c] HM = Horowitz and Metzger.
[d] BD = Borchardt and Daniel (assumed $n = 1$).

step is higher (213 kJ mole^{-1}) than that for the second step (114 kJ mole^{-1}). The early loss of bipy compared with phen in these adducts parallels the boiling points of the two compounds [22]. The magnitudes of the activation energy for the loss of phen and xan groups could be explained from the order of Ni–N and Ni–S bond energies [23]. It is not a conclusive proof, however, of this fact in the absence of other supporting data. Comparison of the E_a for the compounds Ni(bipy)$_3$xan$_2$ and Ni(phen)$_3$xan$_2$ shows that the E_a values are higher for the latter, irrespective of the method of calculation. This may partly be attributed to the structural rigidity of phen as compared with bipy which requires more energy for its rearrangement before undergoing any compositional change.

Satava [11] has presented a series of models on the mechanism of thermal decomposition based on dynamic methods. Recently Nair and Madhusudanan [12] have reported its application to predicting the mechanism of thermal decomposition

TABLE 4

Mechanism of thermal decomposition

No.	Compound	Stage	E_a (kJ mole^{-1})					Remarks *
			From mechanism non-invoking equation		From mechanism based equation			
					(c)	(d)	(e)	
			(a)	(b)				
1	Ni(xan)$_2$		134.6	141.0	125.0	80.7	65.2	c(a, b)
2	Ni(xan)$_2$·phen ether		134.0	157.0	77.2	38.5	20.7	
3	Ni(xan)$_2$·bipy	I	159.0	171.0	160.2	125.7	87.6	c(a)
	ether	II	164.0	99.0	101.0	50.6		c(b)
4	Ni(xan)$_2$·dab	I	176.0	182.0	168.5			c(a)
	ether	II	80.2	80.6	76.7	29.0		c(a, b)
5	Ni(xan)$_2$·en ether		184.0	176.0	170.2	100.1	85.2	c(b)
6	Ni(phen)$_3$xan$_2$	I	213.0	219.0	323.2	181.7	102.0	
		II	114.0	108.0	110.0	80.2	61.0	c(a, b)
7	Ni(bipy)$_3$xan$_2$	I	84.9	175.0	177.6	88.9		c(b)
		II	58.9	36.2	39.9	19.9		c(b)
8	Ni(en)$_3$xan$_2$	I	94.3	99.3	101.2	65.3		c(a, b)
		II	139.3	141.2	156.2	131.2	81.2	c(a, b)

(a) = Freeman and Carroll.
(b) = Horowitz and Metzger.
(c) = Mampel.
(d) = Avrami-I.
(e) = Avrami-II.
* Indicates that the mechanistic and non-mechanistic relations give E_a values which are in agreement. The letters have the meanings indicated above.

of a few coordination compounds. A discussion on the basis of these models has been made for the present series of complexes. Table 4 contains the E_a values obtained from mechanism-invoking and mechanism-independent equations. It shows that the relation from Mample gives the straight line plots for the parameter log g(α) against $1/T$. The table also shows that E_a values calculated from the relation by Freeman and Carroll and by Horowitz and Metzger agreed satisfactorily with that calculated for mechanism-invoking relations. In a few cases, (Ni(xan)$_2$·phen, Ni(phen)$_3$xan$_2$) for the first step, the values of E_a from the Freeman and Carroll, and Horowitz and Metzger relations did differ from those of Mample. The disagreement may be due to the complex overlapping processes of decomposition. It indicates, thus, that the data obtained from the non-mechanistic relations should be tested with those from the mechanism-invoking relations.

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