Journal of Thermal Analysis, Vol. 25 (1982) 463—471

THERMAL ANALYSIS OF HETEROCYCLIC THIONE DONOR COMPLEXES. PART 1

COBALT(II) COMPLEXES OF 1-METHYLIMIDAZOLINE-2(3H)-THIONE

E. S. Raper

School of Chemical & Life Sciences, Newcastle upon Tyne Polytechnic, Newcastle upon Tyne, NE1 8ST England

(Received July 6, 1981)

The thermal decomposition of the Co(II) complexes of 1-methylimidazoline-2(3H)-thione (MImt), general formula $Co(MImt)_2X_2$ (X = Cl, Br & I), have been studied in air and argon by means of TG and DTG as well as in nitrogen by DTA. Quantitative DTA has been used to derive reaction enthalpies (ΔH_R) from the melting and decomposition endotherms in nitrogen. Decomposition processes have been proposed for the complexes in air and in inert atmospheres. A mean coordinate bond dissociation energy ($\bar{D}$) has been estimated for the Co-MImt bond in $Co(MImt)_2Cl_2$.

Reaction end products in air have been identified by X-ray powder diffraction.

There are several reports in the literature devoted to the thermal analysis of metal complexes containing *N*-bonded heterocyclic molecules involving a variety of cations and structural types [1—7]. In contrast to this, little attention has been given to the thermochemistry of complexes wich contain *S*-donating heterocyclic molecules. Some thermal analysis data have been reported for *S*-donating metal complexes of thiourea [8, 9] as well as a kinetic study of some complexes which contain heterocyclic thiol molecules [10].

The coordination chemistry of imidazoline-2-thione (Imt) as well as its *N*(1)-methyl (MImt) (Fig. 1) and *N,N'*(1, 3) di-methyl (DmImt) derivatives towards a variety of metals has recently been established [11—17]. In particular, the interaction of MImt with cobalt(II) halides has been shown to produce pseudo-tetrahedral complexes, $Co(MImt)_2X_2$, in which the ligand is *S*-bonded to the metal [11]. This report is concerned with the thermal analysis of these complexes.

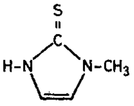

Fig. 1. MImt

Experimental

The complexes were prepared by previously described methods [11] and characterised by a combination of chemical analysis and infrared spectroscopy.

TG and DTG

A Stanton Redcroft TG 750 thermobalance and DTG unit were used together with open Pt crucibles (dia. 6 mm). The furnace atmosphere was column dried (molecular sieve, 13X) flowing air or argon (15 cm^3 min^{-1}). Sample masses varied from 2 to 6 mg; the furnace heating rate was 10°/min^{-1}, recorder speed was 2 mm min^{-1}.

DTA

A Stanton Redcroft 673/4 instrument was used together with quartz crucibles (3 cm (length) *a* 0.3 cm (int. dia.)). The latter were chosen in preference to Pt crucibles because of sample swelling and creep as well as the frequent production of tenacious deposits. The furnace atmosphere was flowing nitrogen 200 cm^3 min^{-1} and the heating rate was 20°/min^{-1}. Sample masses were invariably in the region of 5 mg; the reference material was Al_2O_3 (5 mg also in a quartz crucible). Amplifier sensitivity was 50 μV f.s.d. and the recorder speed was 5 mm min^{-1}.

The relationship:

$$\Delta H = A/K \cdot m$$

where ΔH = specific enthalpy of a standard substance (mJ mg^{-1})
A = peak area of the reaction endotherm (mm^2)
K = calibration constant (mm^2 mJ^{-1}) for a given reaction temperature
m = sample mass (mg)

was used to calibrate the instrument [18] (Table 1).

Table 1

Reference substances for quantitative DTA

Substance	React. temp. C	Specific enthalpy † mJ mg^{-1}	K(calcd)* mm^2 mJ^{-1}
In	156 m	28.47	0.134
$KClO_4$	300 tr	99.28	0.119
Ag_2SO_4	437 tr	57.27	0.109
K_2CrO_4	665 tr	54.34	0.091
Al	660 m	398.1	0.100

m = melting, *tr* = transition.
* mean values, variations from the mean are of the order of $\pm 3-9\%$
† References 4 and 23.

Reaction enthalpies (ΔH_R, kJ mol^{-1}) for the free ligand and the complexes have been derived from the peak areas of the melting and decomposition endotherms by the following relationship:

$$\Delta H_R = A \cdot M/K \cdot m \cdot 10^3$$

where M is the molar mass of the compound and the remaining terms are as defined above. The regular shapes of the melting endotherms generated variations in ΔH_R of the order $\pm 5\%$ ($\pm 2-5$ kJ mol^{-1}); the areas of the broad and occasionally irregularly shaped decomposition endotherms (Fig. 2) however were more difficult to measure and this produced variations in ΔH_R of the order $\pm 10\%$ ($\pm 10-15$ kJ mol^{-1}). These are based on three runs per complex and reflect the overall range of the results. In order to check the calibration for quantitative DTA, enthalpy changes for selected reactions were obtained, also in triplicate, and their mean values, together with literature values are listed in Table 2.

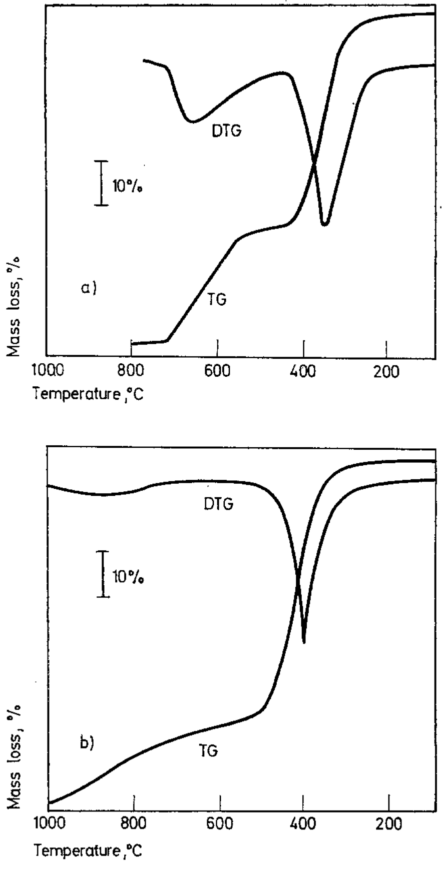

Fig. 2. TG and DTG curves for $Co(MImt)_2Cl_2$ in air (a) and argon (b)

Table 2

Comparison of enthalpy data

Reaction	ΔH_R, [1, 2] kJ mol^{-1}	ΔH_R, (this work) kJ mol^{-1}	T_m, [1, 2] °C	T_m, (this work) °C
$Co(bzt)_2Cl_2(c) \rightarrow CoCl_2(c) + 2bzt(g)$	168.8±3	161.0±10	277	290
$CuSO_4 \cdot 5\,H_2O(c) \rightarrow CuSO_4 \cdot H_2O(c) + H_2O(g)$	217.0±2	230 ±12	102	109
$CuSO_4 \cdot H_2O(c) \rightarrow CuSO_4(c) + H_2O(g)$	69.3±2	67 ± 6	227	240
$Co(py)_2Cl_2$(violet, c) → $Co(py)_2Cl_2$(blue,c)	12.6±0.3	13.1± 1.0	127	120

X-ray powder diffraction

A Guinier-Hägg parafocussing camera, monochromatised CuKα, (λ = 154.05 pm) radiation and Kodirex single-coated X-ray film were employed in identifying the end-products in air; Co_3O_4 (JCPDS reference 9-0418).

Mass spectroscopy

The mass spectrum of $Co(MImt)_2Br_2$ was obtained by direct injection into a Hitachi RMU 6D Mass Spectrometer with an electron impact source and from coupled TG/GC/MS by means of a Stanton Redcroft mass flow thermobalance coupled to a Perkin–Elmer F11 gas chromatograph and a Hitachi RMU 6D Mass spectrometer.

Results and discussion

Data from the TG and DTG curves in air and argon are summarized in Tables 3 and 4; the curves for $Co(MImt)_2Cl_2$ are shown in Fig. 2. Table 5 contains the DTA data, specific DTA curves are shown in Fig. 3.

Table 3

Thermogravimetric analysis in air

Compound	M, gmol^{-1}	Temperature range, T, °C	End product	Overall mass loss, %		Stepped mass losses,	
				Calc.	Obs.	T, °C	%
$Co(MImt)_2Cl_2$	357.9	162–610	Co_3O_4	77.6	76.0	162–374 374–610	43.0 33.0
$Co(MImt)_2Br_2$	446.7	145–618	Co_3O_4	82.1	81.0	145–374 374–618	34.5 46.5
$Co(MImt)_2I_2$	540.7	192–610	Co_3O_4	85.2	85.0	192–502 502–610	48.8 36.2

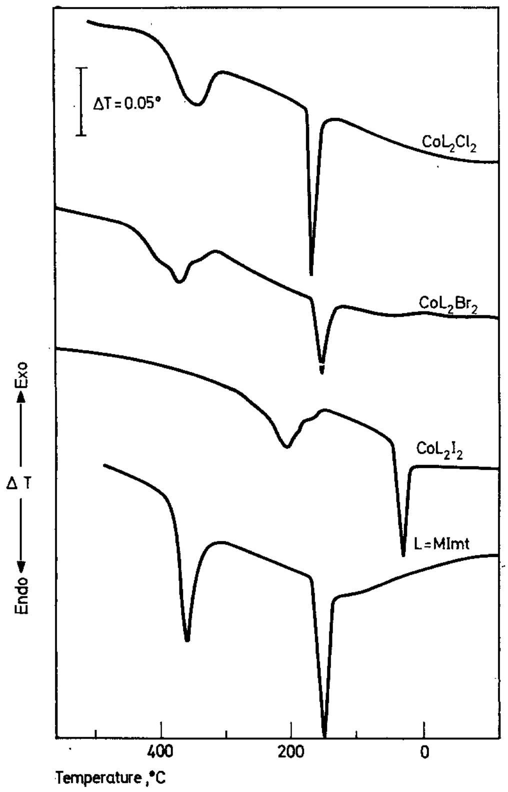

Fig. 3. Selected DTA curves in nitrogen

Table 4

Thermogravimetric analysis in argon

Compound	Temperature range, T °C	Overa mass loss, %	pped mass losses	
			T, °C	%
$Co(MImt)_2Cl_2$	250–1000	78.5	250– 550	58.0
			550–1000	20.5
$Co(MImt)_2Br_2$	250–1000	79.0	250– 550	52.0
			550–1000	27.0
$Co(MImt)_2I_2$	190–1000	85.0	190– 550	60.0
			550–1000	25.0

Table 5

DTA in nitrogen

Compound	Peak temperature, °C			Peak character	Reaction enthalpy ΔH_R, kJmol^{-1}
	T_i	$T_p(T_m)$	T_f		
$Co(MImT)_2Cl_2$	169	185	204	Melting endotherm	31
	341	385	428	Decomposition endotherm	120
$Co(MImt)_2Br_2$	157	169	187	Melting endotherm	35
	341	400	460	Decomposition endotherm	122
$Co(MImt)_2I_2$	80	85	94	Melting endotherm	41
	181	220	260	Decomposition endotherm	147
MImT	133	150	163	Melting endotherm	14
	290	359	428	Vapourisation endotherm	56

T_i, T_p, T_f and T_m refer to the initial, peak, final and mean ($T_m = 1/2(T_i + T_f)$) procedural decomposition temperatures.

T_p refers to the melting point endotherm and T_m refers to the decomposition endotherm.

By using XRPD on the end-products it has been shown that the complexes degrade to the oxide (Co_3O_4), in air, over the temperature range 145 to 618°.

$$3\ Co(MImt)_2X_2(c) + 2\ O_2 \rightarrow Co_3O_4(c) + 6\ MImt(g) + 3\ X_2(g)\ .$$

The agreement between observed and theoretical mass losses for this process is very close and within experimental error (±2%) for all of the complexes.

Analysis of the stepped mass losses for the chloro and bromo complexes suggest that MImt loss occurs in two stages. Two-thirds of the MImt molecules are lost in the first stage and the remainder, together with the halogen atoms are lost in the second (final) stage of the decomposition to the oxide.

The first stage mass loss for the iodo complex (48.8%) significantly exceeds the MImt composition in this complex (41.8%). This suggests that partial decomposition of the metal iodide is included with MImt evolution in this stage of the decomposition; the final stage involves conversion of the residual iodide to Co_3O_4.

The TG and DTG curves in argon differ significantly from those in air. The final mass losses are characterized by gradual downward drifts on the TG curves with no clearly defined end plateaux. The major feature of the DTG curves is a well defined peak in the temperature range 190–550° which coincides with the major mass losses on the TG curves. These mass losses (Table 4) are consistent with the removal of both MImt molecules:

$$Co(MImt)_2X_2(c) \rightarrow CoX_2(c) + 2\ MImt(g)$$

In the case of the iodo complex however the mass loss (60.0%) again exceeds the MImt composition in the complex (41.8%) and suggests that partial decomposition of the metal salt accompanies evolution of the heterocyclic molecules.

Attempts to identify the end products from the reactions in argon, by X-ray powder diffraction, were unsuccessful however, due to the presence of diffuse diffraction lines and considerable background fluorescence.

A combined TG/GC/MS study of the bromo complex showed that the major product was MImt ($m/e = 114$). This suggests that undecomposed MImt molecules are produced in inert almospheres; fractional mass loss in air, on the other hand, probably signifies oxidation of the heterocyclic molecule although it has not been possible to establish this experimentally, at the present time, for these halo complexes. Other cobalt complexes in this series [12] however have produced fractional ligand (MImt) loss, as well as cobalt disulphide, during their thermal degradation in air, which is clearly indicative of MImt decomposition.

The DTA curves in nitrogen (Fig. 3) show clearly that melting and decomposition are separate processes for these complexes. In addition, they indicate that the molten phase is stable over a wide temperature range. The presence of a one-stage decomposition endotherm (180 – 460°) parallels the essentially one-stage decomposition in argon (190 – 550°) and suggests that the decomposition processes are the same in both inert atmospheres.

The total decomposition enthalpies for these complexes are in the range 151 – 188 kJ mol^{-1}. The significantly larger value for the iodo complex probably contains a contribution from the decomposition of the metal iodide as well as from MImt. Because of the lack of decomposition enthalpies for cobalt(II) complexes with other *S*-donating heterocyclic molecules the results from this work have been compared (Table 6) with data from the more extensively studied field of *N*-donating heterocyclic molecules. This serves to place the results from this work in a wider context. Furthermore, the values for the *N*-donating heterocyclic molecules cover a wide range and reflect a corresponding variation in the nature of the metal-ligand bond. The data for the MImt complexes are in the upper portion of the range and, significantly, are closest to those of another *S*,*N*-containing heterocyclic molecule, benzothiazole.

The enthalpy of the gas phase decomposition:

$$\mathrm{Co(MImt)_2Cl_2(g)} \rightarrow \mathrm{CoCl_2(g)} + 2\ \mathrm{MImt(g)}$$

may be estimated by assuming the sublimation enthalpy of the complex to be similar to that of related $\mathrm{CoL_2Cl_2}$ complexes (L is a monodentate heterocyclic molecule); a mean value of 110 ± 15 kJ mol^{-1} has been determined from the literature [2, 3]. Using this value together with the sublimation enthalpy for $\mathrm{CoCl_2}$ (226 ± 4 kJ mol^{-1} [19] and the decomposition enthalpy for the complex (151 ± 10 kJ mol^{-1}) a gas-phase dissociation enthalpy of 267 ± 15 kJ mol^{-1} has been calculated for the above process. This corresponds to twice the mean coordinate bond dissociation energy, $\bar{D}$, [20] of the Co-MImt bond, provided that the complex is monomeric and no other stereochemical changes occur. X-ray studies on related complexes [12, 21, 22] have shown that the complex is likely to be monomeric and have also revealed Co – S(MImt) distances in the range 230.2(1) to 234.0(3) pm.

Table 6

Decomposition enthalpies, kJ mol^{-1} for the process $CoX_2L_2(c) \rightarrow CoX_2(c) + 2L(g)$ [1, 2, 3, 8] (L is a monodentate heterocyclic molecule)

L =	py	α-pic	β-pic	γ-pic	an	box	bzt	MImt
X								
Cl	119.5	109.5	91.5	129.6	148.4	142.5	168.0	151
Br	114.1	88.6	70.6	99.9	—	143.4	160.1	157
I	51.4	51.0	—	45.6	—	—	—	188

py = pyridine;
pic = picoline;
an = aniline;
box = benzoxazole;
bzt = benzothiazole.
Variations in ΔH_R are in the range ±0.5–15.0 kJ mol^{-1}.

Consequently a useful correlation may be made between thermally derived bond energies and bond lengths. In this respect a mean Co(II)–S (thione) bond length of 232(2) pm may be correlated with an estimated mean coordinate bond dissociation energy of 134 ± 15 kJ mol^{-1}.

*

The author is grateful to Mr. J. R. Creighton, Newcastle upon Tyne Polytechnic, for technical assistance with this work and to Dr. F. Buttler, Teesside Polytechnic for mass spectral data and helpful discussion.

References

1. G. Beech, C. T. Mortimer and E. G. Tyler, J. Chem. Soc. (A), (1967) 925.
2. C. T. Mortimer and J. L. McNaughton, Thermochim. Acta, 6 (1973) 269.
3. C. T. Mortimer and J. L. McNaughton, Thermochim. Acta, 8 (1974) 265.
4. J. C. Van Dam, G. Hakvoort, J. C. Jansen & J. Reedijk, J. Inorg. Nucl. Chem., 37 (1975) 713.
5. K. C. Dash and P. Pujari, J. Inorg. Nucl. Chem., 40 (1978) 1173.
6. P. Lumme and M.-L. Korvola, Thermochim. Acta, 9 (1974) 109.
7. P. Lumme and M.-L. Korvola, Thermochim. Acta, 13 (1975) 419.
8. S. J. Ashcroft, J. Chem. Soc. (A), (1970) 1021.
9. H. Janicki, G. Blotny, B. Bator-Sawicka & J. Dobrowolski, J. Thermal Anal., 9 (1976) 401.
10. K. N. Johri, N. K. Kanshik and K. A. Venugopalan, J. Thermal Anal., 10 (1976) 47.
11. E. S. Raper and J. L. Brooks, J. Inorg. Nucl. Chem., 39 (1977) 2163.
12. E. S. Raper and I. W. Nowell, Inorg. Chim. Acta, 43 (1980) 165.
13. E. S. Raper, M. E. O'Neill and J. A. Daniels, Inorg. Chim. Acta, 41 (1980) 145.
14. E. S. Raper, M. E. O'Neill and J. A. Daniels, Inorg. Chim. Acta, 41 (1980) 201.
15. J. Barker and E. S. Raper, Inorg. Chim. Acta, 53 (1981) L177.
16. M. E. O'Neill, E. S. Raper and J. A. Daniels, Inorg. Chim. Acta, 54 (1981) 125.
17. E. S. Raper and P. H. Crackett, Inorg. Chim. Acta, 50 (1981) 159.

18. W. W. WENDLANDT, Thermal Methods of Analysis, 2nd Ed., John Wiley and Sons, New York, 1974.
19. L. BREWER, G. R. SOMAYAJUBE and E. BRACKETT, J. Amer. Chem. Soc., 63 (1963) 11.
20. F. BASOLO and R. G. PEARSON, Mechanism of Inorganic Reactions, Wiley, New York, 2nd Ed., 1967.
21. E. S. RAPER and I. W. NOWELL, Acta Cryst., B35 (1979) 1600.
22. I. W. NOWELL, A. G. COX and E. S. RAPER, Acta Cryst., B35 (1979) 3047.
23. Stanton Redcroft Technical Information Sheet (No. 15) and Consultancy Service.

ZUSAMMENFASSUNG — Die thermische Zersetzung von Kobaltkomplexen des 1-Methylimidazolin-2(3H)-thions (IMmt) der allgemeinen Formel $Co(MImt)_2X_2$ (X = Cl, Br, J) wurde in Luft und Argon mittels TG und DTG und in Stickstoff mittels DTA untersucht. Reaktionsenthalpien (ΔH_r) wurden durch quantitative DTA aus den in Stickstoffatmosphäre erhaltenen endothermen Schmelz- und Zersetzungspeaks erhalten. Es wurden Mechanismen für die Zersetzungsprozesse der Komplexe in Luft und inerter Atmosphäre vorgeschlagen. Die mittelere Dissoziationsenergie ($\bar{D}$) der koordinativen Bindung Co— MImt in $Co(MImt)_2Cl_2$ wurde bestimmt.

In Luft erhaltene Reaktionsendprodukte wurden durch Röntgenpulverdiffraktometrie identifiziert.

Резюме — Изучено термическое поведение комплексов двухвалентного кобальта с 1-метилимидазолин-2(3H)-тионом (МИмт) общей формулы $Co(МИмт)_2X_2$, где X = Cl, Br и I, методами ТГ б ДТГ в атмосфере воздуха и аргона, и методом ДТА в атмосфере азота. Количественный ДТА в атмосфере азота был использован для установления энтальпий реакций (ΔH_R) на основе эндотерм плавления и разложения. Предложены процессы разложения комплексов в атмосфере воздуха и в инертной атмосфере. Найдена средняя энергия диссоциации координационной связи Co-МИмт в комплексе $Co(МИмт)_2Cl_2$. Конечные продукты реакции, проведенной в атмосфере воздуха, были идентифицированы порошковым рентгено-диффракционным методом.