

THERMOCHEMICAL AND SPECTROSCOPIC PROPERTIES OF TRANSITION METAL COMPLEXES

PART III¹. COMPLEXES OF COBALT HALIDES WITH TOLUIDINES

G. BEECH, G. MARR, AND B. W. ROCKETT

The Polytechnic, Wolverhampton (England)

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ABSTRACT

Heats of decomposition and spectroscopic results for some solid toluidine complexes of cobalt halides are reported. The results are interpreted in terms of "Soft and Hard Acid and Base" concepts. The softness of the central metal atom increases as less electronegative ligands are attached. This was supported by measurements of the spectroscopic covalency parameter, B' , which decreases in the order $Cl > Br > I$. Comparisons are made with some previously published data.

INTRODUCTION

Recently¹ we have reported the thermochemical and spectroscopic properties of some cobalt (II) complexes with chloro- and fluoro-substituted anilines. We now report data concerning the thermal decomposition of the analogous toluidine complexes. The toluidines are more basic² than the corresponding halogenated anilines and it would be expected that the complexes should be more covalent. We have also recorded the spectroscopic properties of these complexes, derived apparent crystal-field parameters and attempted to correlate these with the respective heats of decomposition.

EXPERIMENTAL

Preparations

The preparations of the complexes have been described previously³. The compositions were checked by weight-loss measurements (Table I). The compounds were hygroscopic and were stored in a desiccator until required.

Calorimetry

A Perkin-Elmer Differential Scanning Calorimeter (DSC-1B) was used for the thermal measurements. All of the decompositions were carried out under dry nitrogen at a flow-rate of 20 ml. min⁻¹. The samples were encapsulated as previously described⁴ using loose-fitting domed aluminium covers. The measurements of peak areas were made with a planimeter and the calorimeter was calibrated by the heat of fusion of

high purity (99.99%) indium (m.p. 429°K). Uncertainties are quoted as standard deviations of the mean.

TABLE I

HEATS OF DECOMPOSITION OF $\text{Co L}_2 \text{X}_2$

L^a	X	Weight loss (%)		ΔH_1 (kJ mol ⁻¹)	T_i^b	T_p^b	T_f^b
		Obs.	Calc.				
<i>o</i> -Tol	Cl	61.8	62.3	140 ± 4	460	500, 515	555
						520, 535	
<i>m</i> -Tol	Cl	62.5	62.3	162 ± 2	455	520	540
						525	
<i>p</i> -Tol	Cl	62.4	62.3	165 ± 3	460	520	560
<i>o</i> -Tol	Br	49.7	49.5	168 ± 4	470	540	540
<i>m</i> -Tol	Br	23.8 49.6	24.7 49.5	$\left. \begin{array}{l} 102 \pm 3 \\ 40 \pm 2 \end{array} \right\} 142 \pm 4$	470	525	535
					570	595	610
						605	
<i>o</i> -Tol	I	41.0	40.6	168 ± 4	450	490 530, 550	570
<i>m</i> -Tol	I	39.6	40.6	121 ± 4	460	490	545
						540	
<i>p</i> -Tol	I	41.5	40.6	145 ± 4	460	500	555
						520	
						545	
An	Cl			149 ± 2	460	525	570
						555	
An	Br			164 ± 2	440	520	540
An	I			140 ± 4	460	500	525
					490	600	630

^aLigand abbreviations in Tables I-III are as follows: *o*-Tol = *o*-toluidine; *m*-Tol = *m*-toluidine; *p*-Tol = *p*-toluidine; An = aniline; *o*-CIA = *o*-chloroaniline; *m*-CIA = *m*-chloroaniline; *p*-CIA = *p*-chloroaniline. ^b T_i , T_p , and T_f refer to the temperature at which the recorder pen first departs from the baseline, the peak maximum, and the point at which the pen rejoins the baseline.

Spectroscopy

The electronic spectra of the complexes were recorded between $5,000\text{ cm}^{-1}$ and $30,000\text{ cm}^{-1}$ using a Unicam SP700 spectrophotometer. The samples were prepared as Nujol mulls by the method of Wasson⁵. The toluidine complexes possess³ an approximately tetrahedral structure about the cobalt atom and the apparent crystal field parameters were calculated using a tetrahedral model. The absorption bands were usually split by spin-orbit coupling. We have assumed that the numerical averages of the components of each of the two main bands corresponded to the transitions from ${}^4A_2(F)$ to ${}^4T_1(F)$ and ${}^4T_1(P)$ levels and these are referred to as ν_2 and ν_3 , respectively⁶. The calculations of $10D_q$ and B' (Table II) were made with the IBM 1620 Computer at this College.

TABLE II

SPECTROSCOPIC RESULTS AND DERIVED VALUES OF $10D_q$ AND B' FOR $\text{Co L}_2 \text{X}_2$

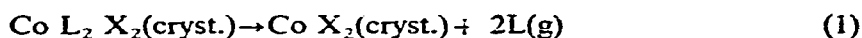
<i>X</i>	<i>L</i>	Components of ν_2 (cm^{-1})	Components of ν_3 (cm^{-1})	$10D_q$ (cm^{-1})	B'
Cl	<i>o</i> -Tol	6,300; 7,600; 8,800	15,950; 17,100	4,403	725
	<i>m</i> -Tol	6,200; 8,350	15,780; 16,240; 17,150	4,228	732
	<i>p</i> -Tol	6,000; 8,000	15,900; 17,200	4,045	760
	<i>p</i> -Tol ^a	6,100; 7,200; 8,600	15,600; 16,200; 17,000	4,240	722
Br	<i>o</i> -Tol	7,400; 9,050	15,410; 16,040; 16,760	4,872	646
	<i>m</i> -Tol	6,700; 8,000	15,250; 16,000; 16,790	4,279	701
	<i>p</i> -Tol	7,700	15,150; 15,950; 16,850	4,507	677
I	<i>o</i> -Tol	6,750; 8,000; 8,400	15,400; 16,200	4,524	662
	<i>m</i> -Tol	6,780; 8,000; 8,380	15,380; 16,100	4,529	658
	<i>p</i> -Tol	6,620; 8,880	14,400; 15,400; 16,200	4,567	623

^aUsing results from Ref. 9.

RESULTS

Thermal measurements

Each of the complexes decomposed, ultimately, to the solid halide by reaction (1) with the exception of

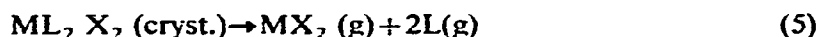


dibromobis(*p*-toluidine)cobalt(II) which evolved white fumes during its decomposition and yielded unidentifiable products. The *m*-toluidine (*m*-Tol) complex, $\text{Co}(\textit{m}\text{-Tol})_2 \text{Br}_2$, decomposed in two stages. The first peak in the thermogram was accompanied by a weight-loss of 23.8% after which a deep blue liquid was formed. Possibly, this decomposition occurred by reactions (2) and (3). It is probable

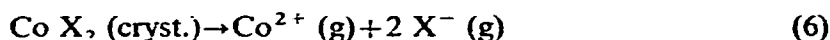
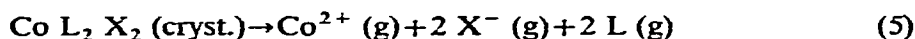


that many of the other decompositions reported here could proceed by a similar route but the thermograms were insufficiently well-resolved to confirm this suggestion. The heats of reaction and temperature parameters are shown in Table I, together with the results for the aniline complexes reported previously^{1a}, for comparison.

Ideally, the heats of reaction should be corrected to the gas phase but this is not possible since the heats of sublimation of $ML_2 X_2$ (cryst.) are not known. The heat of reaction (4), ΔH_4 may be calculated



from a knowledge of the heat of sublimation⁷ of MX_2 . This enthalpy change will differ from the analogous reaction of (4) in which $ML_2 X_2$ is gaseous by the heat of sublimation of the complex but since the complexes are all of a similar structure, it is probable that the variation in heats of sublimation will be small. Also, the heats of reaction (5), ΔH_5 , may be calculated from reactions (1) and (6)⁷.



No attempt has been made to correct the heats of reaction to standard conditions because the heat capacity data are not available. The decompositions all occurred over a similar temperature range so that the corrections would be expected to be small. Some solution calorimetric measurements have been reported by Ablov *et al.*⁸ for certain of these complexes ($X = Cl$; $L = o-, m$ -Toluidine; $X = Br$, $L = p$ -Toluidine; $X = I$, $L = p$ -Toluidine). The values of ΔH_1 were derived by these workers but they are all higher than the values reported here. One possible explanation is that a heat capacity term, which is required for correction to room temperature, may be large. Since it is not possible to measure the heat capacities of the complexes within the range of decomposition, we were not able to correct our measured enthalpy changes.

Spectroscopic measurements

The spectroscopic results are shown in Table II. As an independent check on the validity of our calculations, we have also used some data reported by Ferguson⁹ for single crystals of dichlorobis-(*p*-toluidine)cobalt(II). We used a combination of Ferguson's results for the parallel and perpendicular needle axes since both orientations would be present in milled samples. A comparison of the two sets of results indicates adequate agreement within experimental error.

DISCUSSION

There is no apparent correlation between the values of $10D_q$ and the measured or calculated heats of decomposition. For a particular toluidine complex, we found that ΔH_1 was lowest with $X = I$, and this may indicate a weaker M-N bond in the

iodides if the heats of sublimation are insensitive to the nature of the halogen. A similar generalisation may be made for ΔH_4 and ΔH_5 (Table III), although these energies also reflect changes in M-X bond strengths.

TABLE III
HEATS OF REACTIONS (4) AND (5) FOR $\text{Co L}_2 \text{X}_2$

<i>X</i>	<i>L</i>	ΔH_4 (kJ mol ⁻¹)	ΔH_5 (kJ mol ⁻¹)
Cl	<i>o</i> -Tol	194	777
	<i>m</i> -Tol	212	799
	<i>p</i> -Tol	219	802
	An	203	786
	<i>o</i> -CIA	183	766
	<i>m</i> -CIA	212	795
	<i>p</i> -CIA	218	801
Br	<i>o</i> -Tol	211	779
	<i>m</i> -Tol	195	763
	An	218	786
	<i>o</i> -CIA	212	780
	<i>m</i> -CIA	223	791
	<i>p</i> -CIA	212	780
I	<i>o</i> -Tol	218	769
	<i>m</i> -Tol	171	722
	<i>p</i> -Tol	195	746
	An	190	741
	<i>o</i> -CIA	170	721
	<i>p</i> -CIA	178	729

For a particular halogen, it was not possible to arrange the ligands into identical sequences of apparent M-N bond strengths. For this purpose, we have also calculated the ΔH_4 and ΔH_5 values for the aniline and the chloroaniline complexes of Co X_2 (the fluoroaniline complexes have not been included due to structural differences and the non-availability of data for $\text{X} = \text{I}$). ΔH_4 and ΔH_5 may be arranged into the following sequences:



The first sequence is similar to the sequence of base strengths for protonation². Exact agreement is not expected since small differences in sublimation enthalpies, or structural effects, may easily effect such a sequence. However, the complete lack of correlation when $\text{X} = \text{Br}$ or I leads us to suggest that the substituted anilines are class A (hard) donors¹ and the exchange of $\text{X} = \text{Cl}$ for $\text{X} = \text{Br}$ or I increases the class B nature (softness) of the acceptor. This is not unexpected since nitrogen is not

easily polarisable and the non-planar arrangement about the nitrogen atom does not permit M-N π -bonding.

We were not able to observe any systematic dependence of Δt upon ΔH values. However, the Racah parameters¹¹ (B') were found to decrease in the order



This may indicate greater covalency in the order I > Br > Cl and this increase probably occurs mainly in the M-X bond. This in turn will decrease the positive charge on the cobalt atom and weaken its electrophilic nature. If, as we have suggested, π -bonding is absent in these complexes then this weakened electrophilicity will tend to decrease the M-N bond strength.

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