THE THERMAL DECOMPOSITION OF METAL COMPLEXES—II*

THE DECOMPOSITION OF SOME BISQUINOLINE METAL(II) HALIDES

D. H. BROWN, R. N. NUTTALL and D. W. A. SHARP Chemistry Department, The Royal College of Science and Technology, Glasgow C.1.

(Received 27 July 1963; in revised form 16 December 1963)

Abstract—Bisquinolinemetal(II) halides generally lose one molecule of quinoline on heating to give the monoquinoline complexes. On further heating the manganese and nickel chloride derivatives lose one third of a molecule of quinoline and then decompose to the anhydrous halides. Other monoquinolinemetal(II) halides decompose directly to the anhydrous halides. The co-ordination about the metal atoms in the various complexes has been determined by spectroscopy. The possible structures which may be present are discussed.

QUINOLINE complexes are known for most elements and in the case of the dipositive transition metal halides generally have the stoichiometry MX_2Q_2 (X = halogen, Cl or Br, Q = quinoline). Bisquinolinecobalt(II) chloride undergoes thermal decomposition⁽¹⁾ to monoquinolinecobalt(II) chloride, CoX_2Q , and it has recently been shown that bispyridinenickel(II) chloride undergoes successive thermal decomposition to monopyridinenickel(II) chloride and nickel(II) chloride.⁽²⁾ The purpose of the present work was to study the thermal decomposition of some bisquinolinemetal(II) halides and to deduce from spectroscopic measurements and chemical analysis the nature and possible structures of the thermal decomposition products.

EXPERIMENTAL

Thermal decompositions were carried out on a Stanton Thermal Balance working at a chart speed of 6 in/hr; all thermal decompositions were carried out in air. Samples of thermal decomposition products were subsequently prepared by heating complexes to a pre-arranged temperature in an oven. Reflectance spectra were taken on a Hilger Uvispek Spectrophotometer. All decomposition products were examined by X-ray powder photography using a 9 cm camera and CuK α radiation.

Bisquinolinemetal(II) halides were prepared by two methods. In the first method the hydrated metal halide was dissolved in ethanol and quinoline was added to precipitate the complex which was recrystallized from ethanol. In the second method the hydrated metal halide was refluxed in quinoline for several hours and the precipitated complex was washed successively with hot ethanol and with dry ether. The complexes $CoCl_2Q_2$,^(3,4) $CoBr_2Q_2$,⁽⁵⁾ $NiCl_2Q_2$ (yellow isomer),⁽⁶⁾ NiI_2Q_2 ,⁽⁶⁾ $CuCl_2Q_2$,^(4,7) $ZnCl_2Q_2$,⁽⁸⁾ and $ZnBr_2Q_2$ ⁽⁴⁾ have been previously described in the literature. (Found

* For Part I see D. H. BROWN, R. H. NUTTALL, and D. W. A. SHARP, J. Inorg. Nucl. Chem. 25, 1067 (1963).

- ⁽¹⁾ F. REIZENSTEIN, Z. anorg. Chem. 11, 254 (1896).
- ⁽²⁾ D. H. BROWN, R. H. NUTTALL, and D. W. A. SHARP, J. Inorg. Nucl. Chem. 25, 1067 (1963).
- ⁽³⁾ F. REIZENSTEIN, Ann. 282, 277 (1894).
- ⁽⁴⁾ E. BORSBACH, Ber. Dtsch. Chem. ges. 23, 434 (1890).
- ⁽⁵⁾ H. GROSSMAN and F. HUNSELER, Z. anorg. Chem. 46, 380 (1905).
- ⁽⁶⁾ D. M. L. GOODGAME and M. GOODGAME, J. Chem. Soc. 207 (1963).
- ⁽⁷⁾ B. LACHOWITZ, Monatsh. 10, 884 (1899).
- ⁽⁸⁾ J. V. DUBSKY and V. DOSTAL, Publ. Fac. Sci. Univ. Masaryk. 196, 17/23 (1934).

for bisquinolinemanganese (II) chloride: Mn, 14.6; Cl, 19.0; C, 55.7; H, 3.8; N, 7.4. Calc. for $MnCl_2Q_2$: Mn, 14.3; Cl, 18.5; C, 56.2; H, 3.6; N, 7.3%. Found for bisquinolinecopper(II) bromide: Cu, 13.5; Br, 33.9; C, 44.4; H, 3.0; N, 5.7. Calc. for $CuBr_2Q_2$: Cu, 13.3; Br, 33.3; C, 44.9; H, 2.9; N, 5.8%)

The results of the thermogravimetric studies are given in Table 1. The temperatures quoted are those of the maximum rate of decomposition under the conditions used.

The equivalent weights are those calculated assuming the formula of the starting bisquinolinemetal(II) halide. The process of thermal decomposition was also examined on a Kofler melting point apparatus.

RESULTS

Table 1 shows that thermal decomposition of the bisquinolinemetal(II) halides: MnCl₂Q₂, CoCl₂Q₂, CoBr₂Q₂, NiCl₂Q₂, NiBr₂Q₂, NiBr₂Q₂, CuCl₂Q₂, CuBr₂Q₂, $CuBr_2Q_2$, $CuBr_2Q_2$, Cu

Starting material	Temperature (°C)	Equivalent weights		Resulting	Analysis for metal		Analysis for halogen	
		Found	Theory	compound	Found	Theory	Found	Theory
MnCl ₂ Q ₂	190	257	255	MnCl ₂ Q	21.8	21.6	28.0	27.8
	220	213	212	MnCl ₂ ² Q	25.8	26.0	33.1	33.5
	340	128	126	MnCl ₂	43·3	43.7	56·0	56.3
	600			Mn ₂ O ₃	68.6	69.5		
$CoCl_2Q_2$	280	257	259	CoCl₂Q	22.6	22.8	27·0	27.4
	335	125	130	CoCl ₂	45 ∙0	45.4	53.9	54.6
CoBr ₂ Q ₂	280	345	348	CoBr₂Q	16.6	16-9	45.3	46 ∙0
	335	225	219	CoBr ₂	25.9	27.0	72·0	73·0
NiCl ₂ Q ₂	190	260	259	NiCl ₂ Q	22.8	22.8	27.8	27.4
	245	218	216	NiCl₂ 3 Q	27·0	27 ·3	32.5	32.9
	320	133	130	NiCl ₂	45·1	45.4	53.9	54.6
NiBr ₂ Q ₂	210	348	348	NiBr₂Q	16·7	16.9	45.4	46 ∙0
	270	220	219	NiBr ₂	26.2	27.0	72.1	73·0
NiI ₂ Q ₂	225			NiO	77.4	78·7		
CuCl ₂ Q ₂	245	268	264	CuCl ₂ Q	24·0	24.2	27.2	26.9
	275	138	135	CuCl ₂	47·0	47.4	52.5	52.6
CuBr ₂ Q ₂	240	350	353	CuBr₂Q	18·0	18.1	44 ·8	45 ·3
	310	228	224	CuBr ₂	27.8	28.6	69·2	71.4
ZnCl ₂ Q ₂	260	266	265	ZnCl ₂ Q	24·1	24.5	27.2	26.8
	340	No definite compounds formed						
ZnBr ₂ Q ₂	300	No definite compounds formed						

TABLE 1

 $ZnCl_2Q_2$, and $ZnBr_2Q_2$ give monoquinolinemetal(II) halides in all cases except bisquinolinenickel(II) iodide and bisquinolinezinc(II) bromide. The former complex is oxidized to nickel(II) oxide whilst the latter complex decomposes with charring to give a product which appears to be a mixture of zinc oxide and zinc bromide. Only the yellow form of bisquinolinenickel(II) chloride was studied as the blue tetrahedral form was found to be too unstable to be examined using the present apparatus. Thermal decomposition of the monoquinolinemetal(II) halides CoQ_2Q , $CoBr_2Q$, $NiBr_2Q$, and $ZnCl_2Q$ gives the anhydrous metal halides although these often contain some carbon due to charring in the latter stages of the decomposition. Monoquinolinemanganese(II) chloride and monoquinolinenickel(II) chloride decompose thermally by loss of one out of three molecules of quinoline to give complexes MCl_2^2Q and these subsequently break down to the anhydrous metal chlorides. Manganese(II) chloride ultimately decomposes to dimanganese trioxide.⁽⁹⁾ No definite compounds could be isolated from the thermal decomposition of monoquinolinecopper(ll) bromide.

X-Ray powder photography showed that all of the phases isolated are separate and distinct entities. None of the phases appeared to be isomorphous with one another. The various phases had complex structures and no attempts were made to obtain unit cell dimensions.

Examination of the process of thermal decomposition shows that in most cases the specimens enter a liquid phase on decomposition. This could be due either to true melting or to solution of the product in the liberated quinoline. It is not possible to differentiate between the possibilities but in view of the difference in behaviour of monoquinolinecopper(II) chloride which remains molten over a range of 60° C and monoquinolinenickel(II) chloride which crystallizes from solution almost immediately after the phase change, it is likely that the former is the correct explanation.

The results of spectroscopic examination are summarized and discussed below element by element. All figures are in cm^{-1} . Measurements were only possible down to 10,000 cm⁻¹ using the present apparatus.

Manganese	${}^{4}A_{1g}(G),$	${}^{4}E_{g}(G)$	${}^{4}T_{2g}(G)$	${}^{4}T_{1g}(G)$
MnCl ₂ py ₂ (white)	23,700	20,4	00	19050, 16670(10)
$MnCl_2Q_2$ (white)	23,800	21,2	80 <i>sh</i>	18,350
MnCl ₂ Q (white	23,750	22,1	70	18,690
$MnCl_2 \frac{2}{3}Q$ (white)	23,700	22,4	70	19,800
MnCl ₂ (white)	22,800	22,200		19,000
- · ·	23,700	22,0	00	18,000(10)

The visible spectrum of bisquinolinemanganese(II) chloride is recorded above together with the spectra of its thermal decomposition products. The spectrum of bispyridinemanganese(II) chloride (py = pyridine) and of manganese(II) chloride are included for comparison. Bispyridinemanganese(II) chloride is known to have octahedral co-ordination about the metal atom⁽¹¹⁾ as has manganese(II) chloride.⁽¹²⁾ The spectra of the quinoline derivatives are very similar to those of MnCl₂py₂ and MnCl₂ and are characteristic of manganese atoms in octahedral co-ordination.^(10,13) The ground state for a d^5 atom in an octahedral field is ${}^6A_{1g}$ and the observed bands correspond to transitions to the electronic states given at the head of the columns. The transitions ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$ show a decrease in ligand field strength in the order MnCl₂Q₂ > MnCl₂Q > MnCl₂ > MnCl₂[§]Q. Pyridine exerts a stronger ligand field than does quinoline.

From their spectra and colours all the cobalt(II) quinoline halide complexes examined have tetrahedral co-ordination about the metal. Cobalt(II) chloride and bromide have octahedral co-ordination⁽¹²⁾ about the metal and their spectra are not

⁽⁹⁾ N. SIDGWICK, Chemical Elements and their Compounds, Oxford University Press (1950).

⁽¹⁰⁾ C. K. JørgENSON, Absorption Spectra and Chemical Bonding in Complexes, Pergamon Press, Oxford (1962).

⁽¹¹⁾ E. KÖNIG and H. L. SCHLÄFER, Z. phys. Chem. 26, 371 (1960).

⁽¹²⁾ A. F. WELLS, Structural Inorganic Chemistry (3rd Ed.), Oxford University Press (1962).

⁽¹³⁾ T. M. DUNN, *Modern Co-ordination Chemistry* (Edited by J. LEWIS and R. G. WILKINS) Interscience Publishers, New York (1960).

Cobalt							
$\alpha - \operatorname{CoCl_2py_2} \beta - \operatorname{CoCl_2py_2} CoCl_2Q_2 CoCl_2Q_2 CoCl_2Q CoCl_2^2 - CoCl_4^2 - CoBr_2Q_2 COCl_4^2 - COCl_4^2 - COBr_2Q_2 - COBr_2Q_2 - COBr_2Q_2 COCl_4^2 - COBr_2Q_2 - COBr_2Q_2$	(violet) (blue) (blue) (blue) (blue) (blue)	19050 19050w	18180 17320 17450 16950 16400 16670	16130 ⁽¹⁰⁾ 16000 ⁽¹⁰⁾ 16260 16350 16100 16000	15380 15870 15500 15380	15040 15200 14840	14400 ⁽¹⁰⁾
CoBr ₂ Q CoBr ₄ ²	(blue)		15500	15 <i>3</i> 80 14900	14290	14400	13900(10)

included. The spectra⁽¹⁰⁾ of the two forms of bispyridinecobalt(II) chloride [α -, violet, octahedral; β -, blue, tetrahedral] and the CoCl₄²⁻ and CoBr₄²⁻ ions (tetrahedral) are given for comparison. The ground state for a Co²⁺ ion in T_d symmetry is ${}^{4}A_2$ and electronic spectra at frequencies of the order of 15,000 to 17,000 cm⁻¹ are generally assigned to the transitions ${}^{4}A_2 \rightarrow {}^{4}T_1(P)$, ${}^{2}E(G)$, and ${}^{2}T_1(G)$.

Nickel	${}^{3}T_{1g}(P)$	${}^{1}A_{1g}(G)$	${}^{8}T_{1g}\left(F\right)$ and	$^{1}E_{g}(D)$
NiCl ₂ py ₂				
(yellow)	24100	22990	14100	(2)
NiCl ₂ Q ₂	22730	19230 (sh)	13160	12200
(yellow)	22700	19200 (sh)	13150	12000
NiCl ₂ Q (red)	21140	19200 (sh)	11150	11760
NiCl ₂ ² Q (red)	21650	19230 (sh)	12740	11490
NiCl ₂ (yellow)	22170	19300 (sh)	13000	11700
- 9	22100	19400	12900	11600(10)
NiBr ₂ Q (red)	20000	17700	11360 (sh)	10810
NiBr, (orange)	20830	16670	12200	10470
	20700	16800	12100	10300(10)
NiO	23800	21980	15380	13900
	23900	21200	15200	13900(10)
	Tet	rahedral		
NiBr ₂ O ₂ (blue)	16400	11400 sh	10000	(6)
	16500	11360	10000	

All of the nickel derivatives with the exception of bisquinolinenickel(II) bromide appear to have octahedral co-ordination about the metal. Nickel chloride is known to have such a co-ordination arrangement⁽¹²⁾ and the yellow form of bisquinolinenickel(II) chloride has been investigated previously.⁽⁶⁾ Bispyridinenickel(II) chloride has been shown to have octahedral co-ordination about the metal atom and the spectrum is given for comparison with the spectra of the quinoline complexes. For a d^8 ion in a field of symmetry O_h the ground state is ${}^{3}A_{2g}(F)$ and assignments are made for the observed bands. From the transition ${}^{3}A_{2g}(F) \rightarrow {}^{2}T_{1g}(P)$ the order of ligand field

Copper		
CuCl ₂ py ₂	·	14290(10)
CuBr ₂ py ₂	24390	14290(10)
CuCl ₂ Q ₂	19230	16130
CuCl ₂ Q		12500
CuBr ₂ Q ₂		16670
CuBr ₂ Q	No peak, sl	houlder at 15,800

strength in the various complexes is $\text{NiCl}_2 Q_2 > \text{NiCl}_2 > \text{NiCl}_2 Q_2 > \text{NiCl}_2 Q_2 > \text{NiCl}_2 Q_2$. The band which occurs near 19,000 cm⁻¹ is assigned to the transition ${}^3A_{2g}(F) \rightarrow A_{1g}(G)$ in agreement with DUNN⁽¹³⁾ as the energy of this band appears little dependent upon the ligand field of the complex. Bisquinolinenickel(II) bromide has recently been shown to contain nickel atoms in tetrahedral co-ordination; the spectrum observed in the present work is in close agreement with that recorded previously.⁽⁶⁾

As is general with copper(II) salts bispyridinecopper(II) chloride has a distorted octahedral co-ordination about the copper atom.⁽¹⁴⁾ The d-d transitions in the spectra of copper(II) salts tend to be swamped by charge-transfer bands and the origin of the present bands is not clear. No definite information, therefore, can be deduced as to the stereochemistry about the copper atom in these complexes.

It is not possible to obtain information on the structure of the zinc complexes from their ultra-violet or visible spectra. From partial structure determinations bispyridine-zinc(II) chloride and bromide are considered to have tetrahedral co-ordination about the zinc atoms.⁽¹⁵⁾ Zinc chloride has a tetrahedral co-ordination about the metal and zinc bromide has an octahedral co-ordination about the metal.

DISCUSSION

From the preceding results it can be stated that the quinoline complexes of manganese(II) and nickel(II) chlorides together with monoquinolinenickel(II) bromide have octahedral co-ordination about the metal. The quinolinecobalt chlorides and bisquinolinenickel(II) bromide have tetrahedral co-ordination about the metal. The co-ordination arrangements in the copper and zinc complexes are not known.

The geometrical formulation of the monoquinoline complexes with tetrahedral co-ordination about the metal is simple in terms of dimeric or of polymeric molecules. The octahedral complexes are rather more difficult to formulate. GILL and NYHOLM⁽¹⁵⁾ have postulated a simple polymeric chain for the basic structure of the violet form of bispyridinecobalt(II) chloride and similar structures are likely for the bisquinolinemetal(II) halides. Possible structures have been briefly suggested for monopyridinenickel(II) chloride⁽²⁾ and similar structures are likely for the monoquinolinemetal(II) halides. The complexes of stoicheiometry $MX_{23}Q$ necessarily have more complex structures and it is not possible to write down a structure in which all of the metal atoms have the same environment. Simple models of the required stoicheiometry may be built up, however, by cross-linking chains of the type required for the stoicheiometry MX₂Q. The halides which are formed after complete decomposition of the bisquinolinemetal(II) halides (except zinc chloride which has a different arrangement of atoms) have layer structures in which each halogen is acting as a bridge between three metal atoms, the metal atom being in octahedral co-ordination.⁽¹²⁾ This suggests that the compounds formed as intermediates during the thermal decompositions have similar structures with halogen atoms also acting as bridges between three metal atoms.

In view of the necessity to postulate very different structures for the various types of quinolinemetal halide complex and the possibility of different geometrical arrangements in complexes of different metals it is perhaps not unexpected that the observed

⁽¹⁴⁾ J. D. DUNITZ, Acta Cryst. 10, 307 (1957).

⁽¹⁵⁾ N. S. GILL and R. S. NYHOLM, J. Inorg. Nucl. Chem. 18, 88 (1961).

order of ligand field strength for the various types of complexes is not the same when comparing one metal with another. The overall results suggest that pyridine exerts a stronger ligand field than quinoline. This is probably due to steric factors controlling the ability of the smaller pyridine molecule to approach closer to the metal ion and is also reflected in the relative values of pK α (for pyridine pK $\alpha = 5.23$, for quinoline pK $\alpha = 4.94$).⁽¹⁶⁾ In spite of the necessity to postulate structures for the MX₂²/₃Q complexes with not all of the metal atoms having the same environment, the spectra of those complexes are distinct and the units of the structure must be sufficiently small that the effect of all of the ligands in the repeating unit are felt by all of the atoms in the unit.

Acknowledgement—We thank the Department of Scientific and Industrial Research for the award of a Senior Fellowship (to R. H. N.). We thank Messrs. T. BOYLE and J. MACPHERSON for technical assistance.

⁽¹⁶⁾ A. ALBERT, R. GOLDACRE and J. PHILLIPS, J. Chem. Soc. 2240 (1948).