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# Thermal and spectroscopic study of palladium(II) halide complexes with diethyl quinolylmethylphosphonates (DQMP)

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## Abstract

Thermal (DTA, TG) and spectroscopic (IR, UV–VIS) studies of palladium(II) dihalide complexes, $Pd(dqmp)_2X_2$, and tetrahalogenopalladium salt complexes, $[Hdqmp]_2[PdX_4]$ ($X = Cl$ or Br), of diethyl 2- and 8-quinolylmethylphosphonates (2-dqmp and 8-dqmp) have been carried out in order to understand the decomposition of these biologically active compounds. Comparing the thermal behaviour of 2-dqmp and 8-dqmp complexes, great differences were observed, especially between the quinolinium salt complexes. On heating to about 100°C, the 8-dqmp salt complexes were converted into the corresponding hexahalogenodipalladium salt complexes, $[H8\text{-}dqmp]_2[Pd_2X_6]$. The thermal and spectral properties of all the complexes with respect to their cytostatic activity have been discussed.

## INTRODUCTION

In the last few years, a great number of palladium(II) halide complexes of various ligands which are important in medical and biological systems, have attracted particular interest [1–6]. Recently, we reported the preparation, and some spectroscopic studies and X-ray crystal-structure determinations, of palladium(II) halide complexes with diethyl esters of 2- and 8-quinolylmethylphosphonic acids (2-dqmp and 8-dqmp) [7,8]. The preliminary screening tests showed that these complexes exhibit some cytostatic activity on an epidermoid human carcinoma (KB cell) and on murine leukaemia (L1210) cell line. It is known that the Pd(II), like Pt(II), can act in DNA regions [9,10], and that the breaking ability of the Pt,Pd–X bonds is important for the reaction mechanism in the cell. When the halogen is lost with greater ease, a higher cytotoxicity of the complex can be expected. The great differences reported in the cytostatic activities of the complexes suggested the investigation of their thermal stability. The results deduced thermogravi-

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metrically were subsequently confirmed by the infrared and electronic spectral studies.

## EXPERIMENTAL

The neutral palladium(II) dihalide complexes, $Pd(dqmp)_2X_2$, as well as the ion-pair tetrahalogenopalladium(II) salt complexes, $[Hdqmp]_2[PdX_4] \cdot 2H_2O$ (X = Cl, Br), of diethyl 2- and diethyl 8-quinolylmethylphosphonates were prepared using the methods previously described [7,8].

The thermogravimetric analyses (TGA) were carried out on a recording Cahn RG electrobalance in an air atmosphere at a heating rate of 4° C $min^{-1}$ up to about 800° C, using 3–5 mg of sample in quartz crucibles.

Differential thermal analyses (DTA) were made on a Netzsch diferential thermal analyser. DTA curves were obtained in static air atmosphere, with samples of varying weights (30–60 mg), at a heating rate of 5° C $min^{-1}$ from ambient temperature to 800° C. The reference substance was pure alumina.

Infrared spectra were recorded on a Perkin–Elmer 580B spectrophotometer in KBr discs (4000–250 $cm^{-1}$) and as Nujol mulls in polyethylene (400–200 $cm^{-1}$).

The ultraviolet–visible spectra were obtained in dimethylformamide solution with a Cary Model 17 spectrophotometer in the range 40000–15000 $cm^{-1}$.

The X-ray powder diffraction patterns were taken with a Philips counter diffractometer (monochromatised Cu K$\alpha$ radiation).

## RESULTS AND DISCUSSION

Diethyl quinolylmethylphosphonates (2-dqmp and 8-dqmp) are ligands with two potential donor atoms, quinoline nitrogen and phosphoryl oxygen. While 2-dqmp can act as monodentate N-bonded or as bidentate N,O-bonded chelate ligand-forming complexes with 1 : 2 and 1 : 1 metal-to-ligand ratios, 8-dqmp binds palladium ion only through the nitrogen atom. In HX acidic media, both ligands form salt complexes with the protonated quinolylmethylphosphonate ligand as cation and the tetrahalogenopalladium(II) complex as anion. Some differences were observed between the corresponding molecular and ionic 1 : 2 complexes of 2-dqmp and 8-dqmp with respect to their physical properties, some spectral and structural data, and also their biological activity [7,8]. Comparing their thermal behaviour, considerable differences were also observed, especially for the tetrahalogenopalladium(II) salt complexes. By refluxing in methanol, the 2-dqmp salt complexes decompose to the molecular dihalogenopalladium(II) complexes, while the 8-dqmp salt complexes are converted into the corresponding hexahalogenodipalladium(II) salt complexes. The mode of decomposition of these complexes was followed by the thermal analyses and by some of the spectroscopic studies.

## *Thermal studies*

The most significant thermal data of the complexes obtained from the corresponding TG and DTA curves are summarised in Table 1 and presented in Figs. 1 and 2. From the TG curves, it can be seen that the thermal decompositions of the neutral dihalogenopalladium(II) complexes are very similar. All the complexes are anhydrous, and the dehalogenation processes overlap partly with those corresponding to the pyrolysis of the ligands. The absence of a stable intermediate species makes it impossible to propose tentative pyrolytic decomposition mechanisms for these complexes. On the bases of the initial decomposition temperatures, which correspond to the beginning of the dehalogenation process, the thermal stability of the complexes follows the order $Pd(8\text{-dqmp})_2Br_2 < Pd(8\text{-dqmp})_2Cl_2 < Pd(2\text{-dqmp})_2Br_2 < Pd(2\text{-dqmp})_2Cl_2$. For each of these complexes, the dehalogenation process appears on the DTA curve as an endothermic effect centred at 130, 170, 215 and 225 °C, respectively, and corresponds with the melting point values published in the literature [7,8]. It can be concluded that the 8-dqmp complexes are less stable than the corresponding chloride complexes, followed by the bromide complexes and the corresponding chloride complexes. These results are in good agreement with those obtained

TABLE 1

TG and DTA data for palladium(II) halide complexes

| Complex | Dehydration | | Dehalogenation and pyrolysis | |
|---|---|---|---|---|
| | $H_2O$ [a] (%) | Temp. range, TG (°C) | Temp. range, TG (°C) | $T$, DTA [b] (°C) |
| $Pd(2\text{-dqmp})_2Cl_2$ | – | – | 190–751 | 225, 300 |
| $Pd(2\text{-dqmp})_2Br_2$ | – | – | 172–727 | 215 |
| $Pd(8\text{-dqmp})_2Cl_2$ | – | – | 153–732 | 170 |
| $Pd(8\text{-dqmp})_2Br_2$ | – | – | 121–788 | 130 |
| $[H2\text{-dqmp}]_2[PdCl_4]\cdot 2H_2O$ | 4.40<br>(4.26) | 73–100 | 110–755 | 115, 130 |
| $[H2\text{-dqmp}]_2[PdBr_4]\cdot 2H_2O$ | 4.09<br>(3.52) | 34–65 | 100–635 | 100, 150 |
| $[H8\text{-dqmp}]_2[PdCl_4]\cdot 2H_2O$ | 4.57<br>(4.26) | 40–94 | 130–723 | 130 [c], 170, 175 |
| $[H8\text{-dqmp}]_2[PdBr_4]\cdot 2H_2O$ | 3.73<br>(3.52) | 40–100 | 134–720 | 130 [c], 160, 170 |

[a] Calculated values are given in parentheses.

[b] DTA peaks above about 300 °C are diffuse.

[c] Conversion of tetrahalogenopalladium complex into hexahalogenodipalladium complex.

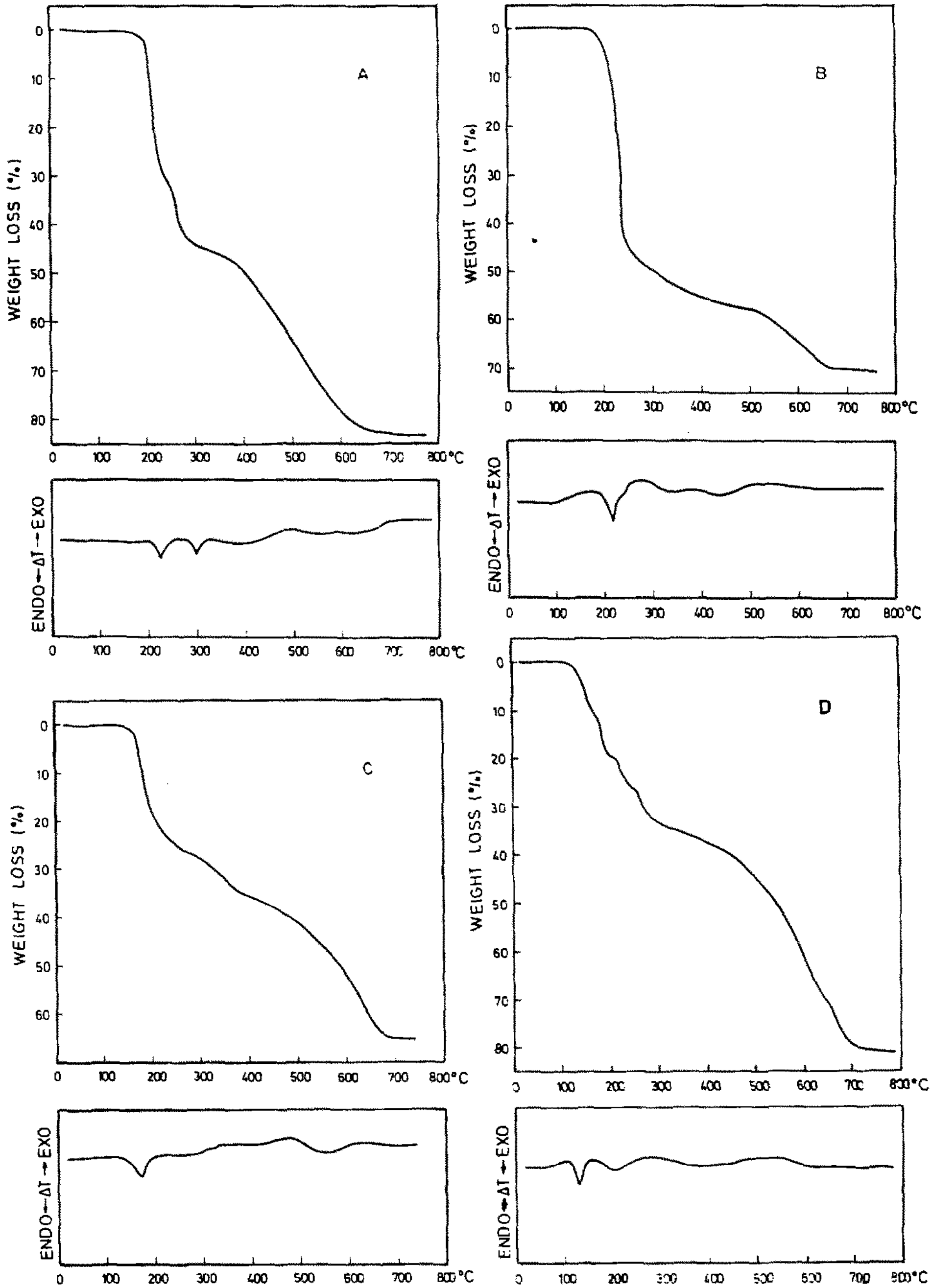

Fig. 1. TG–DTA curves for: A, $Pd(2\text{-dqmp})_2Cl_2$; B, $Pd(2\text{-dqmp})_2Br_2$; C, $Pd(8\text{-dqmp})_2Cl_2$; D, $Pd(8\text{-dqmp})_2Br_2$.

for their cytostatic activity. It has been suggested that the requirements for a potential anti-tumour coordination compound are a pair of strongly covalently bonded ligands, with nitrogen being the donor atom, and a pair of

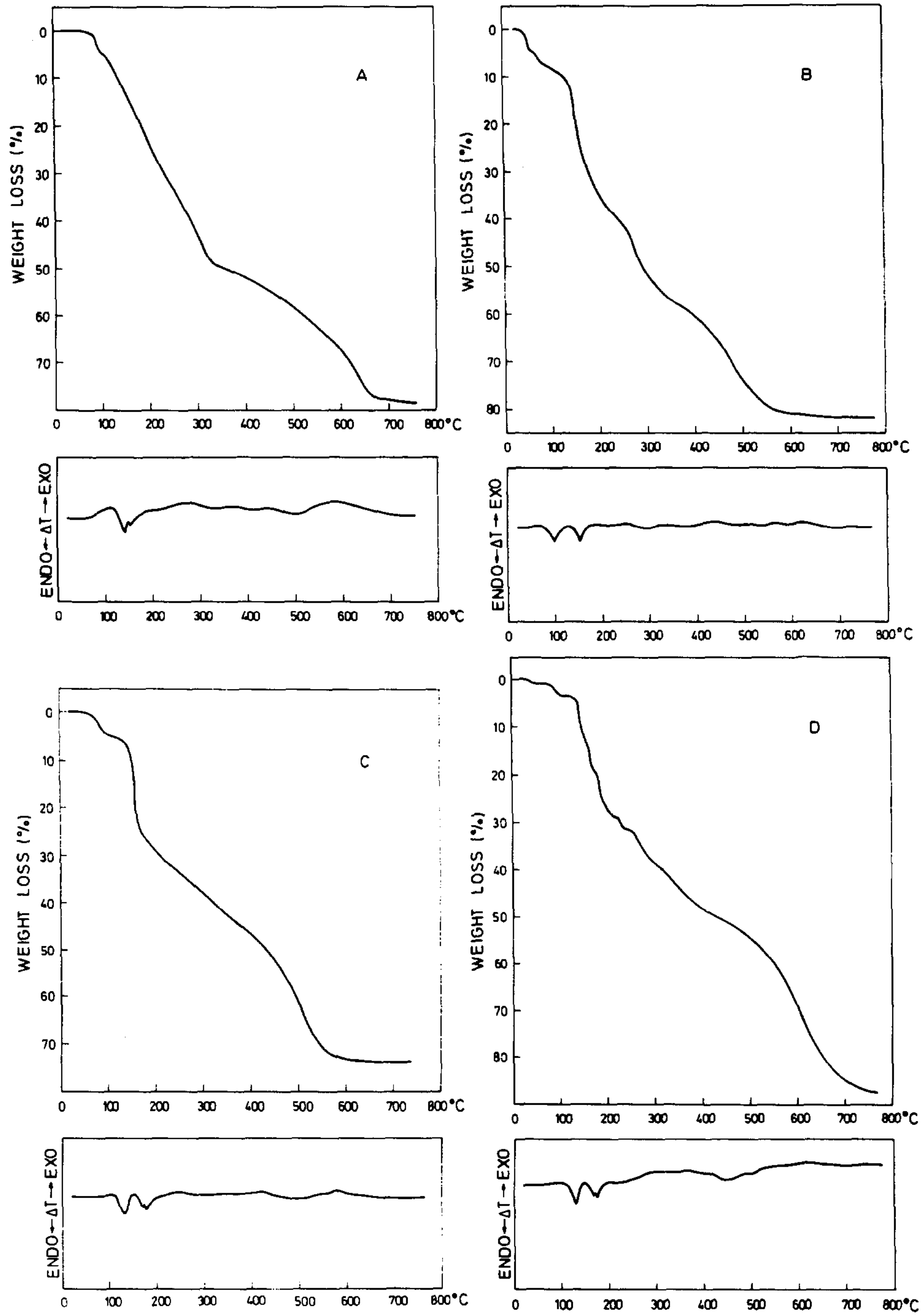

Fig. 2. TG–DTA curves for: A, $[H2\text{-}dqmp]_2[PdCl_4]\cdot 2H_2O$; B, $[H2\text{-}dqmp]_2[PdBr_4]\cdot 2H_2O$; C, $[H8\text{-}dqmp]_2[PdCl_4]\cdot 2H_2O$; D, $[H8\text{-}dqmp]_2[PdBr_4]\cdot 2H_2O$.

moderately labile ligands such as halides [11]. In general, when the leaving ability of the labile ligands is lower, a smaller anti-tumour effect of the complex is observed.

All tetrahalogenopalladium salt complexes are hydrated and exhibit a single, somewhat broad, dehydration step over the range 34–100 °C. The low temperatures of water loss indicate that it is lattice held. Dehydration is immediately followed by the dehalogenation process, visible in the DTA curves as an endothermic effect. No stable intermediates are obtained for the 2-dqmp salt complexes. They decompose in a curve with inflections but without a distinct plateau. We cannot assign a stoichiometric compound to the curve inflections, although heating in most solvents results in very stable neutral dihalogenopalladium complexes. It has been shown by solid-phase thermal transformation that some tetrahalogenoplatinum(palladium) salt complexes of various amine, pyridine and quinoline derivatives also yield neutral Pt,Pd(II) dihalide complexes [12,13].

In contrast, the TG curves of the 8-dqmp salt complexes indicate an intermediate product stable in the 100–130 °C region, formed according to the reaction

$$2[\mathrm{H8\text{-}dqmp}]_2[\mathrm{PdX}_4] \rightarrow [\mathrm{H8\text{-}dqmp}]_2[\mathrm{Pd}_2\mathrm{X}_6] + [\mathrm{H8\text{-}dqmp}]\mathrm{X}_2$$

The effect of total dehalogenation of the complexes is not observed, due to its overlapping with the ligand degradation processes. The final pyrolytic residue of all the complexes obtained after heating up to 800 °C was considered, from their infrared spectra and X-ray diffraction patterns, to be a mixture of metallic Pd and $P_2O_5$. Considerable differences were obtained between the calculated and found residue values, because of the partial sublimation of $P_2O_5$ which takes place above 300 °C [14].

## *Spectroscopic studies*

The thermal decomposition of the complexes was also examined by investigating their infrared spectra in order to reveal some characteristics of their thermal behaviour. Our earlier papers describe the infrared spectral data of the free diethyl quinolylmethylphosphonates and their palladium(II) halide complexes [7,8]. This report concentrates on the far-IR region which contains vibrations of the metal–ligand bands (see Table 2).

Dihalogenopalladium complexes show one band for Pd–X and one band for Pd–N stretching vibrations, as expected for trans-square-planar complexes of $D_{2h}$ stereochemistry [15]. In the 2-dqmp complexes, these vibrations appear at higher frequencies than in the spectra of the corresponding 8-dqmp complexes, confirming the assumptions that the halogens are strongly bonded to the palladium ion in these complexes. Furthermore, it is shown that the complexes are completely dehalogenated in the range 230–

TABLE 2

Selected spectral data for the complexes ($cm^{-1}$)

| Complex | Far-IR data [a] | | UV–VIS data [b] $\lambda_{max}$ (log $\varepsilon$) |
|---|---|---|---|
| | $\nu$(Pd–X) | $\nu$(Pd–N) | |
| Pd(2-dqmp)$_2$Cl$_2$ | 352 m | 272 w-m | 37453 (4.00), 34602 (3.96), 33898 (3.95), 33112 (4.00), 32573 (sh, 3.96), 31746 (4.01), 25380 (2.39) |
| Pd(2-dqmp)$_2$Br$_2$ | 321 w | 270 w-m | 37736 (4.34), 33989 (sh, 4.17), 32786 (4.20), 31545 (4.18), 25000 (2.74) |
| Pd(8-dqmp)$_2$Cl$_2$ | 340 m | 260 w | 36101 (4.06), 33333 (3.92), 31746 (3.76) |
| Pd(8-dqmp)$_2$Br$_2$ | 285 w | 260 w | 36630 (4.24), 33333 (3.91), 31746 (3.87), 24631 (2.89) |
| [H2-dqmp]$_2$[PdCl$_4$]·2H$_2$O | 325 m-s | – | 37453 (4.09), 34722 (3.99), 34246 (3.98), 33112 (4.01), 32573 (sh, 3.97), 31746 (4.03), 22624 (2.39) |
| [H2-dqmp]$_2$[PdBr$_4$]·2H$_2$O | 252 m | – | 37807 (4.49), 33898 (sh, 4.40), 33112 (4.31), 31746 (4.24), 24631 (3.26), 21321 (sh, 3.79) |
| [H8-dqmp]$_2$[PdCl$_4$]·2H$_2$O | 320 s | – | 36496 (4.10), 33333 (3.90), 31746 (4.76), 29762 (3.17), 23256 (2.39) |
| [H8-dqmp]$_2$[PdBr$_4$]·2H$_2$O | 247 s | – | 35461 (4.15), 33333 (sh, 3.91), 31898 (3.51), 23923 (3.30), 19231 (2.55) |
| [H8-dqmp]$_2$[Pd$_2$Cl$_6$] | 320 s<br>249 m | – | 36101 (4.12), 33333 (3.90), 31751 (3.84), 29698 (3.26), 23240 (2.45) |
| [H8-dqmp]$_2$[Pd$_2$Br$_6$] | 257 s | – | 36630 (4.23), 33333 (sh, 3.92), 31847 (3.91), 23923 (3.58), 19231 (2.62) |

[a] Nujol mulls in polyethylene (400–200 $cm^{-1}$).

[b] In dimethylformamide (40000–15000 $cm^{-1}$).

300 °C. At the same time, the ligand molecules start to decompose by loosing ethyl esters groups, as indicated by the changes in the spectra around 1150 and 1000 $cm^{-1}$, where bands arising from various modes of the P–O–Et group are present. The complexes decompose to a mixture of inorganic materials at 350–420 °C.

All tetrahalogenopalladium complexes are hydrated. The loss of water was indicated in the infrared spectra of complexes as KBr pellets stored for 24 h at 100 °C: the rather intense bands in the 3200–3480 $cm^{-1}$ range disappeared. X-ray diffraction study showed that the water molecules are slightly hydrogen-bonded to the protonated quinoline nitrogen and the phosphoryl oxygen atom [8]. The far-IR spectra of the tetrahalogenopalladium salt complexes show a band at the position expected for terminal halides in square-planar $[PdX_4]^{2-}$ ions with $D_{4h}$ stereochemistry [15,16]. Heating the ionic 8-dqmp complexes converts them to the corresponding hexahalogenodipalladium complexes; these have more complex spectra as there are two types of halide ligands in these dimeric palladium complexes: those that are bridging and those which occupy terminal positions. A bridging vibration would be located at frequencies lower than those for terminal vibrations. The sharing of halogens between two metals in a bridged structure causes the bridged bond to be weaker than a terminal metal–halogen bond. Two bands are found in the spectrum of the chloride complex, while only one is observed for the bromide complex as the other bands are expected to be below 200 $cm^{-1}$.

The electronic spectra of palladium(II) halide complexes of 2-dqmp and 8-dqmp complexes recorded in dimethylformamide show several band maxima in the UV–visible region, the positions of which, along with their extinction coefficients, are given in Table 2. All palladium complexes are diamagnetic with a square-planar geometry and, therefore, three spin-allowed transitions are expected, corresponding to the transitions from the three lower lying d-levels to the empty $d_{x^2-y^2}$ orbitals. The ground state is $^1A_{1g}$ and the excited states are $^1A_{2g}$, $^1B_{1g}$ and $^1E_g$, in order of increasing energy [17]. The absorption spectra of all the complexes show several strong absorption bands in the ultraviolet region, but their detection is complicated, as quinoline ligands alone exhibit intense bands due to $\pi$–$\pi^*$ transitions in almost the same region. The relatively pale colour of the dihalogenopalladium complexes indicates that dqmp ligands have a low ligand field strength in forming these complexes. It can be seen that some absorption bands in the spectra of the palladium bromide complexes occur at lower energies than those of the chloride complexes, as expected from the lower position of bromide in the spectrochemical series, as well as from their various optical electronegativities. Furthermore, it is noteworthy that the intensity of the absorption bands is generally higher for bromide complexes than for their chloride analogues; this can be ascribed to the increased ligand participation in the occupied MO-levels, derived mainly from the metal d-levels. The relatively dark colour of the tetrahalogenopalladium and hexahalogenodipalladium salt complexes indicates a strong charge-transfer absorption originating in the ultraviolet and trailing off well into the visible region [17,18]. In general, the two species $[PdX_4]^{2-}$ and $[Pd_2X_6]^{2-}$ exhibit maxima at the same wavelengths although the latter contains two types of halide ligands, bridging and terminal. An approximately square plane of halide ligands is maintained around the metal, and the d–d transitions which are based mainly on the metal are not strongly affected by the differences in the two types of halides. The extinction coefficients of the maxima of the dimeric ions are, in most instances, approximately double those of the monomeric species.

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