

Absorption Spectra of Osmium(III), Osmium(IV) and Platinum(VI) Mixed Halide and Hexaiodide Complexes

CHR. KLIXBÜLL JØRGENSEN

Cyanamid European Research Institute, Cologne (Geneva), Switzerland

Solution spectra of OsI_6^{3-} , OsI_6^{2-} , the complex $\text{OsCl}_x\text{I}_{6-x}^{2-}$ prepared by Nyholm *et al.*, OsCl_6^{3-} , *trans*- $\text{PtCl}_4\text{Br}_2^{2-}$ are reported and discussed. Reflection spectra and crystallographic data for salts of the Os(IV) chloro-iodo ion are given.

The electron transfer spectra of the low-spin $5d^4$ system OsI_6^{2-} and low-spin $5d^5$ system OsI_6^{3-} are of considerable theoretical interest. Hence, the previous measurements¹ have been extended. Fenn, Nyholm, Owston and Turco² prepared a remarkable complex $\text{OsCl}_x\text{I}_{6-x}^{2-}$ which is further studied with regard to spectroscopic and crystallographic behaviour. Finally, one of the few well-defined $5d$ group mixed halide complexes is *trans*- $\text{PtCl}_4\text{Br}_2^{2-}$ of which the solution spectrum is studied.

Osmium(IV) and osmium(III) hexaiodides. The very narrow $[\pi^{24}(\text{even } \gamma_5)^4] \rightarrow [\pi^{23}(\text{even } \gamma_5)^5]$ electron transfer bands¹ of OsI_6^{2-} and the similar $[\pi^{24}(\text{even } \gamma_5)^5] \rightarrow [\pi^{23}(\text{even } \gamma_5)^6]$ bands of OsI_6^{3-} are of theoretical interest⁴ owing to the strong relativistic effects (spin-orbit coupling) found in the π^{23} configuration. They were hence studied once more. Table 1 and Fig. 1 show that OsI_6^{2-} has an additional, relatively weak electron transfer band at 9350 cm^{-1} . This is a lower wavenumber than the first such band³ of Cs_2RhCl_6 at $10\,000 \text{ cm}^{-1}$, and the lowest known. The band of OsI_6^{2-} was not readily observed¹ with a Beckman DU spectrophotometer but was clearly resolved in carefully adjusted cells of equal water concentration on the Cary 14. We propose to change the previous nomenclature¹ such that this evidently parity-forbidden band is called I (there is a shoulder at $10\,700 \text{ cm}^{-1}$ which however, may be an internal transition in $(\text{even } \gamma_5)^4$ as discussed below) whereas the three strong band groups are called II, III, and IV, in analogy with the several MBr_6 spectra. There are good reasons to believe⁴ that these bands are caused by electron transfer from the following orbitals mainly concentrated on the ligands:

were tried on Os(IV). OsCl_6^{2-} gives immediately a brown (dilute it is straw-yellow) solution of Os(III). This is characterized by the complete absence of the line-group ⁶ at $17\,240\text{ cm}^{-1}$ and a broad band ($\delta(-) = 1500\text{ cm}^{-1}$) at $22\,400\text{ cm}^{-1}$ presumably being a spin-allowed (even γ_5) \rightarrow (even γ_3) transition ($\epsilon = 40$) in analogy ⁷ to that of RuCl_6^{3-} at $19\,200\text{ cm}^{-1}$. A weak band at $17\,700\text{ cm}^{-1}$ ($\epsilon = 5$) of Os(III) in 8 M HCl is possibly a $^2\Gamma_5 \rightarrow ^4\Gamma$ spin-forbidden transition.

OsBr_6^{2-} reacts rather slow with tin(II) in hydrobromic acid, thereby forming an orange solution with a broad band $\sim 21\,400\text{ cm}^{-1}$. It does not have exactly the same spectrum as OsBr_6^{3-} prepared by Ag reduction ¹ (*cf.* also potentiometric measurements ⁸). The solutions of OsI_6^{2-} described in the experimental section do not seem to react with the brown solution of tomato-red SnI_2 dissolved in excess of HI. However, it was found that solutions of chromium(II) or titanium(III) in HI can reduce dilute solutions (*e.g.* below 1 mM) of OsI_6^{2-} though the resulting solutions are not stable for more than a few days but deposit Os. The spectroscopic measurements of solutions which had been reduced with Cr(II) were not entirely satisfactory because the Cr(III) formed by the reaction is green and more strongly coloured than $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. It is possibly $\text{Cr}(\text{H}_2\text{O})_5\text{I}^{2+}$ or $(\text{H}_2\text{O})_4\text{Cr}(\text{OH})_2\text{Cr}(\text{H}_2\text{O})_4^{4+}$. The solutions reduced with Ti(III) were clear red; previously, only a dull grayish yellow colour had been noticed ¹.

The spectrum of such a pink solution in 1 M KI and 0.5 M HI is shown on Fig. 2. In this comparatively simple, low-spin d^5 system, more bands are observed than expected ^{1,4}, actually, the solution must contain a mixture of several Os(III) complexes. If it is saturated with KI, it turns strawberry-pink and has the spectrum also given in Fig. 2 with fewer absorption bands. This is believed to be the genuine OsI_6^{3-} whereas the other absorption bands at $20\,200$ and $23\,400\text{ cm}^{-1}$ are caused by other species such as $\text{OsI}_5(\text{H}_2\text{O})^{2-}$. The conspicuous doublet structure seen in OsI_6^{2-} (Fig. 1) is also apparent in OsI_6^{3-} .

Mixed osmium (IV) chloro-iodides. Whereas OsCl_6^{2-} and OsBr_6^{2-} are very readily prepared, even by reduction of OsO_4 (the similar statement is not true ¹ for RuCl_6^{2-}), OsI_6^{2-} is a rather fugitive species which tends to form blue and green decomposition products. Strong excess of I^- makes sometimes a slow,

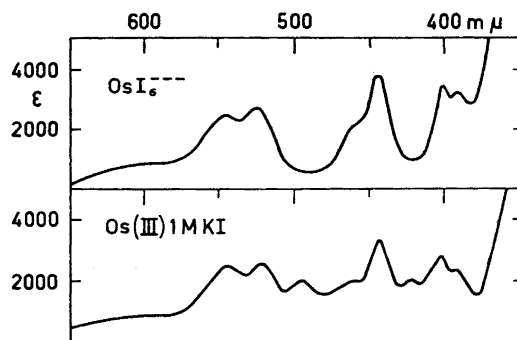


Fig. 2. Absorption spectra of the solutions of Os(III) in saturated KI (0.5 M HI) and in 1 M KI, 0.5 M HI, reduced with Ti(III) as described in the text.

reversible formation of the violet OsI_6^{2-} possible. Fenn, Nyholm, Owston and Turco² investigated the reduction of OsO_4 in acidic solutions containing Cl^- and I^- . Rallo⁹ has recently used electrophoresis to separate the reaction products which fall into three classes: a green hydrolysis product, possibly $\text{I}_5\text{OsOOsI}_5^{4-}$, the violet OsI_6^{2-} , and a blue-green mixed complex $\text{OsCl}_x\text{I}_{6-x}^{2-}$ which syncrystallize with K_2OsCl_6 . The latter complex is remarkably resistant to aquation. The previous authors^{1,9} believe that $x = 3$ or 4. The present writer feels that x may be 5, but does not have certain proof. It might be expected that $\text{OsCl}_5\text{I}^{2-}$ would be more similar to OsCl_6^{2-} with regard to high activation energy for aquation than any other mixed complex. However, a particular *trans*-effect may reverse this argument. As shortly noted by Fenn *et al.*², the analytical composition of $\text{K}_2\text{OsCl}_x\text{I}_{6-x}$ may vary, and by repeating their preparation, we have arrived at an average value of $x \sim 5.9$ rather than ² $x = 5.75$. We did not succeed a complete separation by fractionated crystallization; curiously enough, the cesium salt precipitated by a small amount of Cs^+ seems to concentrate the blue-green iodo complex compared to the subsequent fractions.

The absorption spectrum of the mixed complex given in Fig. 1 is somewhat different from that reported,² since we could find no strong band of the mixed complex in the near infra-red. The weak band $\sim 885 \text{ m}\mu$ is presumably the internal (even γ_5)⁴ transition in the preponderant species OsCl_6^{2-} superposed upon a possibly intensified (because less spin-forbidden) similar transition in $\text{OsCl}_x\text{I}_{6-x}^{2-}$. The theoretical interpretation of the shoulders and the two maxima in the visible is not quite easy. If $x = 5$, the single iodide ligand would be expected¹ to show three one-electron energies, π ($\omega = 3/2$), π ($\omega = 1/2$) and σ ($\omega = 1/2$) where ω is the appropriate double-group quantum number in linear symmetries. If the π - σ energy difference is large, the two former energies are expected to be separated by the amount ζ_{5p} of iodine atoms, that is some 5000 cm^{-1} . However, the bands observed are all concentrated within a narrow range of some 4000 cm^{-1} . This might be taken as an argument for $x = 4$ or 3, but the difficulty subsists that now a complicated structure is expected centered around these baricenters separated by 5000 cm^{-1} . The problem* for $x = 5$ is essentially analogous to that of $\text{Ru}(\text{NH}_3)_5\text{Br}^{2+}$ and $\text{Ru}(\text{NH}_3)_5\text{I}^{2+}$ which were expected to show two transitions from the π orbitals of the halogen to the hole in the lower sub-shell, again separated by ζ_{np} , whereas indeed only one such band is observed¹⁰. Dark purple $\text{Cs}_2\text{OsCl}_x\text{I}_{6-x}$ shows nearly the same absorption bands (at $950, 920, 655, 600,$ and $520 \text{ m}\mu$) as the blue-green ion in solution; the black silver(I) and olive-brown thallium(I) compounds look more or less as the pure Ag_2OsCl_6 and Tl_2OsCl_6 superposed a weak set of bands. Mixed halide complexes are relatively unknown in the platinum group whereas the labile $\text{UCl}_x\text{Br}_{6-x}^{2-}$ have been studied¹¹. Müller¹² has recently separated $\text{ReCl}_x\text{Br}_{6-x}^{2-}$ by electrophoresis, and also $\text{OsCl}_x\text{Br}_{6-x}^{2-}$ seem to be capable of this treatment. However, there is one category which can be directly synthesized:

* If the blue-green species dissolved in 1 M HCl is reduced with Ti(III) , the brown solution shows a weak shoulder at $595 \text{ m}\mu$ and a band at $420 \text{ m}\mu$ (δ (+) $\sim 2000 \text{ cm}^{-1}$ with a shoulder at $376 \text{ m}\mu$. This solution is reversibly oxidized to the original Os(IV) complex by air.

Table 2. Absorption spectrum of *trans*-PtCl₄Br₂²⁻. Notation as in Table 1.

Assignment	λ (m μ)	σ (cm ⁻¹)	$\delta(-)$ (cm ⁻¹)	ϵ
¹ I ₁ → ³ I ₄ ?	((505))	19 800	900	37
even π Br - γ_3	(410)	24 400	1500	200
odd π Cl - γ_3 ?	(263)	38 000	4400	6 600
odd σ Br - γ_3 ?	~ 192	~52 000	—	~21 000

trans-Dibromotetrachloro platinum(IV) ions. The square-planar platinum(II) complexes PtCl₄²⁻, Pt(NH₃)₄²⁺, Pt en₂²⁺ and Pt(CN)₄²⁻ add halogen molecules Y₂ in *trans*-position to form complexes of the general type PtX₄Y₂. The relatively rapid equilibrium established with the free halogens is one of the complicating factors for reaction kinetics where both Pt(II) and Pt(IV) are present. Table 2 gives the absorption bands (nearly all shoulders) of *trans*-PtCl₄Br₂²⁻. In a certain sense, this spectrum is not extremely characteristic; the many weak features look very much as a superposition of PtCl₆²⁻ and PtBr₆²⁻, but this is not exactly the case. The very broad shoulder ~ 263 m μ probably hides the weaker bands expected at slightly lower energy.

PtCl₆²⁻ forms PtI₆²⁻ by a first-order reaction with I⁻, and it is not possible to detect any intermediate complexes. We were not successful in preparing *trans*-PtCl₄I₂²⁻, a black material always precipitated from aqueous solutions of I₂ and PtCl₄²⁻ (traces of ethanol forms Pt and acetaldehyde).

Crystallographic measurements. By the same methods as discussed in the paper on crystalline 5d group hexahalides,¹³ Miss E. Rittershaus here at *CERI* determined unit cell parameters *a* of the cubic antifluorite structure A₂MX₆. Fenn, Nyholm, Owston and Turco² reported that their K₂OsCl_nI_{6-n} had *a* expanded to 9.87 Å from its ordinary value = 9.73 Å. We found that our (less iodide-containing) cesium salt has *a* = 10.26 Å (Cs₂OsCl₆ has¹³ *a* = 10.23 Å) whereas no perceptible difference was found in the thallium(I) salt (9.80 Å).

EXPERIMENTAL

For the absorption spectra, a 0.001 M solution of OsI₆²⁻ was made from one part 0.1 M OsO₄ in H₂O added to 99 parts of 1 M KI, 0.5 M HI, 0.02 M ascorbic acid. Contrary to indications in literature, the solution of OsO₄ is very stable if kept in a brown bottle and made from carefully purified water.

The reduction to Os(III) iodides was made with 10 M HI in which chromium powder (Merck) was dissolved, or with 5 M HI in which titanium powder (Fluka) formed violet Ti(III). In the latter case, a trace of fluoride was necessary as a catalyst for dissolving the metal.

The absorption spectra of solutions were measured on a Cary 14 recording spectrophotometer.

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Received November 25, 1962.