

Die Meßergebnisse an einigen neu untersuchten Diphenylverbindungen (Dinaphthyläther, Biphenylphenyläther) lassen zwar eine befriedigende Deutung mit verschiedenen Modellvorschlägen zu, bei Hydrochinon-

diphenyläther und Resorcindiphenyläther, besonders aber bei 4,4'-Dibromdiphenylsulfid und Phenoxathiin sollte dagegen eher eine Umklappung des Moments annehmen sein.

Comment on: "I.R. Absorption Spectra of Platinum (II) Nitrohalides in the NaCl-Prism Range" and an Assignment of the Anomalous NO_2^- -Vibrations in the Complexes

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(Z. Naturforsch. 17 a, 98 [1962]; eingegangen am 21. November 1961)

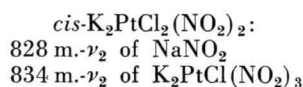
BABAEVA and KHARITONOV¹ report considerable fine structure in the ν_2 (bending) region of the NO_2^- ion in various platinum (II) nitrohalides, but do not attempt to assign these bands. An assignment of these bands is given below.

(a) The ν_2 Satellites

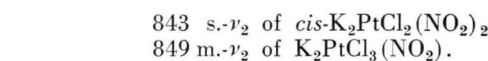
(i) The platinum-chloride-nitrite complexes: The occurrence of so many satellite bands in the ν_2 (bending) region of these nitrite complexes is puzzling, especially in the spectrum of $\text{K}_2\text{PtCl}_3(\text{NO}_2)$. It was pointed out by KETELAAR and SCHUTTE² that the sharp ν_2 -vibration can readily be used for the identification of the alkali nitrites. It is here suggested that the strongest band in the I.R. spectrum of each complex¹ must be assigned to the ν_2 -vibration of the ion in the complex. This leads to the following assignment:

	$\text{K}_2\text{Pt}(\text{NO}_2)_4$	$\text{K}_2\text{PtCl}(\text{NO}_2)_3$	$\text{cis-K}_2\text{PtCl}_2(\text{NO}_2)_2$	$\text{K}_2\text{PtCl}_3(\text{NO}_2)$
$\nu_2 \text{ cm}^{-1}$	840	832	843	849

Consequently, the satellite bands of ν_2 in each complex must be due to either coupling between the NO_2^- vibrations in the unit cell, or impurities. An analysis of BABAEVA's spectra immediately shows that the second possibility explains the observed satellite bands. For example, the following satellites are found in the spectrum of



¹ A. V. BABAEVA and Y. Y. KHARITONOV, Russ. J. Inorg. Chem. 6, 1196 [1960].



The presence of the impurities can be accounted for in two ways: The method of synthesis of these complexes is such that although the average constitution of the complex may be, say, $\text{K}_2\text{PtCl}_2(\text{NO}_2)_2$, the real composition is a mixture of the abovenamed complexes. In addition, these complexes are not very stable and can take part in exchange-reactions with the NaCl (or KBr) during the mulling-operation². This then also accounts for the 828 cm^{-1} band, which can be assigned to the ν_2 -vibration of NaNO_2 (l. c.²). The reaction-scheme is, for example:



(ii) The platinum-bromide (iodide) nitrite complexes: The same applies in this case. A possible assignment is:

	$\text{trans-K}_2\text{PtI}_2(\text{NO}_2)_2$	$\text{cis-K}_2\text{PtBr}_2(\text{NO}_2)_2$	$\text{trans-K}_2\text{PtBr}_2(\text{NO}_2)_2$
$\nu_2 \text{ cm}^{-1}$	836	840	839

(b) The ν_3 - (asymmetric stretching) region: The situation is less clear in this region because of the high intensities and the overlapping of the broad bands. The band which occurs at ca. 1386 cm^{-1} in practically all the spectra can be assigned to a NO_3^- vibration (MASLAKOV³ showed that KNO_2 is invariably contaminated by KNO_3).

No unambiguous assignment of the ν_3 -satellite bands can be given, although the following assignment is indicated by the analysis:

	$\text{K}_2\text{Pt}(\text{NO}_2)_4$	$\text{K}_2\text{PtCl}(\text{NO}_2)_3$	$\text{cis-K}_2\text{PtCl}_2(\text{NO}_2)_2$	$\text{K}_2\text{PtCl}_3(\text{NO}_2)$
$\nu_3 \text{ cm}^{-1}$	1413	1434	1400	1421

It is clear from the assignments given above that in the spectra of the platinum (II) nitrohalides the satellite bands around ν_2 and ν_3 which were reported by BABAEVA and KHARITONOV¹ are due to impurities.

² J. A. A. KETELAAR and C. J. H. SCHUTTE, Rec. Trav. Chim. 80, 721 [1961].

³ I. MASLAKOV, Z. Phys. 51, 696 [1928].

BERICHTIGUNG

Zu HJ. MATZKE, Diffusion von Kr-85 in ThO_2 , Band 16 a, 1255 [1961].

Auf Seite 1256, linke Spalte, zweite Zeile, muß von $n=1$ bis $n=\infty$ summiert werden.

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