

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 anzunehmen sein.

**Comment on: "I.R. Absorption Spectra of Platinum (II) Nitrohalides in the NaCl-Prism Range" and an Assignment of the Anomalous  $\text{NO}_2^-$ -Vibrations in the Complexes**

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

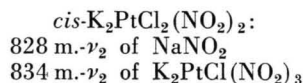
BABAEVA and KHARITONOV<sup>1</sup> report considerable fine structure in the  $\nu_2$  (bending) region of the  $\text{NO}_2^-$  ion in various platinum (II) nitrohalides, but do not attempt to assign these bands. An assignment of these bands is given below.

(a) *The  $\nu_2$  Satellites*

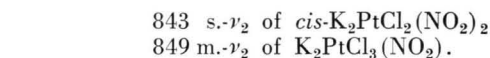
(i) The platinum-chloride-nitrite complexes: The occurrence of so many satellite bands in the  $\nu_2$  (bending) region of these nitrite complexes is puzzling, especially in the spectrum of  $\text{K}_2\text{PtCl}_3(\text{NO}_2)$ . It was pointed out by KETELAAR and SCHUTTE<sup>2</sup> that the sharp  $\nu_2$ -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 complex<sup>1</sup> must be assigned to the  $\nu_2$ -vibration of the ion in the complex. This leads to the following assignment:

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

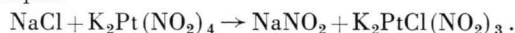
Consequently, the satellite bands of  $\nu_2$  in each complex must be due to either coupling between the  $\text{NO}_2^-$  vibrations in the unit cell, or impurities. An analysis of BABAEVA's spectra immediately shows that the second possibility explains the observed satellite bands. For example, the following satellites are found in the spectrum of



<sup>1</sup> 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-operation<sup>2</sup>. This then also accounts for the 828  $\text{cm}^{-1}$  band, which can be assigned to the  $\nu_2$ -vibration of  $\text{NaNO}_2$  (l. c.<sup>2</sup>). The reaction-scheme is, for example:



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

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

(b) The  $\nu_3$ - (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  $\text{cm}^{-1}$  in practically all the spectra can be assigned to a  $\text{NO}_3^-$  vibration (MASLAKOV<sup>3</sup> showed that  $\text{KNO}_2$  is invariably contaminated by  $\text{KNO}_3$ ).

No unambiguous assignment of the  $\nu_3$ -satellite bands can be given, although the following assignment is indicated by the analysis:

	$\text{K}_2\text{Pt}(\text{NO}_2)_2$	$\text{K}_2\text{PtCl}(\text{NO}_2)_3$	<i>cis</i> - $\text{K}_2\text{PtCl}_2(\text{NO}_2)_2$	$\text{K}_2\text{PtCl}_3(\text{NO}_2)$
$\nu_3$ $\text{cm}^{-1}$	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  $\nu_2$  and  $\nu_3$  which were reported by BABAEVA and KHARITONOV<sup>1</sup> are due to impurities.

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

<sup>3</sup> I. MASLAKOV, Z. Phys. 51, 696 [1928].

## BERICHTIGUNG

Zu HJ. MATZKE, Diffusion von Kr-85 in  $\text{ThO}_2$ , Band 16 a, 1255 [1961].

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

Nachdruck — auch auszugsweise — nur mit schriftlicher Genehmigung des Verlags gestattet

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