

# INFRARED SPECTRA OF METAL-REINECKE COMPOUNDS

By

V. NIKOLÁSEV, J. A. SZABÓ and G. SZEPESSY

Institute of Pathophysiology, Medical University, Szeged and Institute of Organic Chemistry, Attila József University, Szeged, Hungary

(Received: December 1, 1970)

The infrared spectra of the Reineckates of metal ions, amines and complex ions have been studied. It was found that in the infrared spectra of Reineckates of metal ions the C—N band splits into multiplets depending on the electropositivity of the metal ion in the outer sphere.

It is known that Reinecke salt forms stable compounds with metal ions, alkaloids, antibiotics and complex ions [1—7]. CSÁSZÁR [8] has reported on a study of the physico-chemical properties of the Reineckates of transition metal ions. He studied the UV spectra of Reineckates of saturated and unsaturated metal ions in solution, their reflexion spectra, and also their magnetic properties. The results were interpreted on the basis of the ligand field theory. TAKEUCHI and SAITO [9] determined the bond distances in several Reineckates. In a study of the infrared spectra of thiocyanate complexes, NAKAHARA and co-workers [10] stated that in cobalt(III)-hexamine complexes the N—H stretching frequency depends on the outer sphere. Relying upon this experimental fact we found it interesting to study the infrared spectra of some Reineckates.

## Experimental

The Reinecke salt  $\text{NH}_4[\text{Cr}(\text{NCS})_4(\text{NH}_3)_2\text{H}_2\text{O}]$  was a Reanal product of A. R. grade. Preparation of the respective Reineckates was carried out according to literature data [8, 11]. Acidic (HCl) or neutral solutions of the corresponding components were allowed to react, the precipitate was filtered, washed with water and ethanol, and dried over anhydrous  $\text{CaCl}_2$  and  $\text{P}_2\text{O}_5$ .

The IR spectra were taken as follows: samples were prepared in Merck Uvasol KBr. Spectra were registered by a Zeiss UR—10 spectrophotometer.

## Discussion

IR spectral data of Reineckates of amines are summarized in Table I.

It can be seen that in the case of Reineckates of amines all the vibrations appear at the same frequency and the  $\gamma\text{C}\equiv\text{N}$  vibrations is a singlet.

In the case of Reineckates of different metal ions marked differences are found in several bands. The most striking feature is that the  $\gamma\text{C}\equiv\text{N}$  band appears as a multiplet for all compounds. The  $\delta\text{NCS}$  band similarly appears as a doublet.

Table I

IR spectral characteristics of Reineckates of amines (400—3500  $\text{cm}^{-1}$ )

	$\nu\text{C}\equiv\text{N}$	$\delta_a(\text{NH}_3)$	$\delta_s(\text{NH}_3)$	$\rho_r$	$\delta\text{NCS}$
<i>n</i> -butylamine-R	2090	1590	1270	694	480
triethylamine-R	2085	1600	1270	700	490
8-hydroxyquinoline-R	2085	1603	1275	705	480
pyridine-R	2090	1595	1260	698	490
piperidine	2085	1612	1263	700	490



Table II

IR spectral characteristics of Reineckates of metal ions (400—3500  $\text{cm}^{-1}$ )

	$\nu(\text{NH}_3)$	$\nu\text{C}\equiv\text{N}$	$\delta_a(\text{NH}_3)$	$\delta_s(\text{NH}_3)$	$\rho_r(\text{NH}_3)$	$\delta\text{NCS}$
AqR	3450—2750	2120, 2105, 2090	1620	1390	720	455, 425
CdR <sub>2</sub>	3430—3000	2135, 2080	1605	1275	720	503, 460
PbR <sub>2</sub>	3450—3000	2125, 2030	1605	1270	715	505, 462
TlR	3450—3050	2120, 2050	1610	1268	718	505, 465
HgR <sub>2</sub>	3400—3050	2160, 2055, 2075	1607	1276	700	500, 472
CuR <sub>2</sub>	3430—3000	2112, 2088	1610	1260, 1270	700	492, 470
NH <sub>4</sub> R · H <sub>2</sub> O	3500—2750	2110, 2050	1660	1265	700	485



The frequencies of  $\nu\text{C}\equiv\text{N}$  and  $\delta\text{N}-\text{C}-\text{S}$  bands of Reineckates of different cobalt(III)-amine complexes do not differ markedly from those of amines, and similarly to them do not show multiplets. IR spectral data are shown in Table III.

The effect of the outer ion on the  $\nu\text{C}\equiv\text{N}$  stretching frequency can be well interpreted by TAKEUCHI and SAITO's results on bond distances [9]. With decreasing C—S bond distances in Reineckates of pyridine and choline, the N—C bond distance simultaneously increases. Thus, the N—C and C—S distances vary depending on the cation in the outer sphere of the Reineckate.

Table III

IR spectral characteristics of Reineckates of some Co(III)-amine complexes (400—5000  $\text{cm}^{-1}$ )

	$\nu(\text{NH}_3)$	$\nu\text{C}\equiv\text{N}$	$\delta_a(\text{NH}_3)$	$\delta_s(\text{NH}_3)$	$\rho_r(\text{NH}_3)$	$\delta\text{NCS}$
[Co(NH <sub>3</sub> ) <sub>6</sub> ]R <sub>3</sub>	3400—2900	2095	1610	A 1270, 1255R	705	492
[Co(NH <sub>3</sub> ) <sub>5</sub> (NO <sub>2</sub> )]R <sub>2</sub>	3400—2900	2090	1610	A 1320, 1265R	700	492
[Co(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>2</sub> ) <sub>2</sub> ]R	3400—2900	2070	1630	A 1320, 1295R	705	495



A = ammine of the complex

R = ammine of the Reineckate

In the case of the metal ions studied by us with outer ions silver(I), cadmium(II), lead(II), thallium(II), mercury(II) and copper(II), the  $\nu\text{C}\equiv\text{N}$  band was split into doublets or multiplets. This splitting into multiplets can be interpreted by the mutual effect  $\text{Cr}-\text{N}^{(+)}-\text{C}-\text{S}^{(-)}\dots\text{Me}^{(n+)}$ . This interaction is different in the case of cadmium(II), lead(II), and copper(II) ions when  $\nu\text{C}\equiv\text{N}$  is a doublet, and in the case of silver(II) and mercury(II) compounds which show a triplet.

In Reineckates of complexes and amines there is no splitting, since the electropositivity of the outer ions is rather small. From the spectral data obtained, it can be stated that the splitting of the  $\nu\text{C}\equiv\text{N}$  band in Reineckates depends on the electropositivity of the outer ion.

## ИНФРАКРАСНЫЕ СПЕКТРЫ РЕЙНЕКАТОВ СОЕДИНЕНИЙ МЕТАЛЛОВ

*Велимир Николашев, Йозеф А. Сабо и Габор Сенеши*

Авторы изучали инфракрасные спектры различных рейнекатов. Было установлено, что в инфракрасных спектрах рейнекатов полоса  $\nu\text{C}\equiv\text{N}$  распадается в зависимости от электроположительности иона металла в внешней сфере.

### References

- [1] Christensen, O. T.: J. prakt. Chem. **45**, 356 (1892).
- [2] Goupechoux, M.: J. pharm. Chim. **30**, 118 (1930).
- [3] Carlson, H., P. Neumann: J. prakt. Chem. **147**, 38 (1936).
- [4] Kum-Tatt, L.: Nature **182**, 658 (1958).
- [5] Fried, J., O. Wintersteiner: Science, **104**, 273 (1946).
- [6] Carlson, H., F. Rathmann: J. prakt. Chem. **147**, 29 (1936).
- [7] Schmidt—Hebbel, H., P. A. Benavides: Pharm. Zentralhalle **79**, 526 (1938).
- [8] Császár, J.: Magy. Kém. Folyóirat **75**, 47 (1969).
- [9] Takeuchi, Y., Y. Saito: Bull. Chem. Soc. Japan **30**, 319 (1957).
- [10] Nakahara, A., Y. Saito, H. Kuraya: Bull. Chem. Soc. Japan **25**, 331 (1952).
- [11] Várhelyi, Cs., I. Soós, G. Boda: Acta Phys. et Chem. Szeged **13**, 103 (1967).