

UV-Spectra of Acetonyl Acetonate Complexes of Tervalent Metals

In a previous communication¹⁾ it has been shown by BASU and CHATTERJEE that the UV-spectra of a number of bivalent metal chelates can be explained on the assumption that the atomic orbitals of the central metal atom are suitably disposed to form π -bonds in conjugation with C=C and C=O bonds of the ligand molecule. In order to test the usefulness of the assumption further, the work has been extended to the acetonyl acetonate complexes of a number of tervalent metals. Kozo SONE²⁾ has reported that the absorption spectra of these chelates cannot be correlated with their stabilities. Tervalent chromium in d^2sp^3 hybridised state can form three strong π -bonds with d^3 atomic orbitals. So if such π -bonds exist in acetonyl acetonate complex of chromium, the complex with the structure (fig. 1) is expected to show strong forward shift in the $275\text{ m}\mu$ ligand band. In fact the chromium complex in alcoholic solution

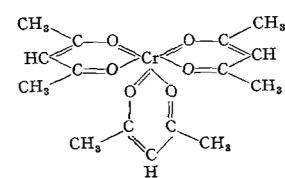


Fig. 1. Acetonyl acetonate complex of chromium

shows an absorption band at $335 \text{ m}\mu$, indicating the existence of π -bonds mentioned above. Along with this forward shift, chromium complexes show a backward shift with an absorption band at $255 \text{ m}\mu$, similar to that observed in the copper complexes. This indicates that along with the structure with doubly linked chromium, singly bonded co-valent structure also makes appreciable contribution to the overall structure of the molecule.

Acetonyl acetonate complex of tervalent cobalt shows only backward shift with one band at $257 \text{ m}\mu$ and the other at $230 \text{ m}\mu$. The $257 \text{ m}\mu$ band is similar to the one observed in the case of chromium and may safely be ascribed to the singly linked co-valent structure of the complex. Since there is no forward shift the π -bonded structure makes no contribution what-so-ever. Right at this moment we are not in a position to make any assignment to the $230 \text{ m}\mu$ band of the complex. The $275 \text{ m}\mu$ legand band is not affected in any way in the complexes of tervalent iron, aluminium and manganese. This evidently proves that as compared to the free state the legand molecule does not find itself in any different surroundings inside these complexes, or in other words these complexes are ionic.

Magnetic measurements also show that the complexes of iron, aluminium and manganese are ionic. But the magneto-chemical measurements class all the acetonyl acetonate metal complexes as ionic³⁾, which, however, is not consistent with their absorption spectra. Spectrophotometry appears to be a better method in classifying these metal chelates into ionic and co-valent groups.

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¹⁾ BASU, S., and K. K. CHATTERJEE: Naturwiss. **42**, 413 (1955).

²⁾ KOZO SONE: J. Amer. Chem. Soc. **75**, 5207 (1953).

³⁾ MARTELL and CALVIN: Chemistry of Metal Chelate Compounds. New York: Prentice Hall Inc. 1952.