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Electronic Absorption Spectrum of Tris(2,2′-bipyridine)-cobalt(I) Complex

Youkoh KAIZU, Yasuo TORII and Hiroshi KOBAYASHI

Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

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Very recently electronic absorption spectral studies have appeared on the lower valent tris-(2,2′-bipyridine)-complexes.[1–3] In these lower valent complexes, 'metal to ligand' charge-transfer bands are observed in the near infrared and visible region. In previous papers,[2,3] it was shown that the charge-transfer transitions can be identified since they give rise to a different spectral behavior from those of the (π,π^*) transition of the coordinating ligand or the (d,d^*) transition in the central metal ion, when a small perturbation such as methyl-substitution is introduced into the system of bipyridine.

In this note, a small perturbation technique was applied for assignment of the lower wave number absorption bands.[2,3] Figure 1 shows absorption spectra of the tris-bipyridine complexes of cobalt(I). The absorption bands were observed at 7200, 16400 and 26200 cm^{-1}. The 16400 cm^{-1} band is the same as the result of qualitative measurement by Waind and Martin,[4] who overlooked the 7200 and 26200 cm^{-1} bands and reported quite different ultraviolet spectrum[5] from ours. The lowest wave number band observed at 7200 cm^{-1} behaves as 'ligand to metal' charge-transfer band upon the dimethyl-substitutions. The band at 7200 cm^{-1} is shifted in the order: 4dmbip[*1] (6700 cm^{-1}), bipy (7200 cm^{-1}), 5dmbip[*1] (7500 cm^{-1}). On the contrary, the ultraviolet band is shifted in the order: 5dmbip (33200 cm^{-1}), bipy (34200 cm^{-1}), 4dmbip (34300 cm^{-1}). This indicates that the band observed at *ca.* 34000 cm^{-1} should be assigned to a (π,π^*) transition of the coordinating bipyridine. Martin *et al.*[5] reported the lowest (π,π^*) transition of the coordinating bipyridine at 35200 cm^{-1}. However, we observed the band at 34200 cm^{-1} when the solution of higher concentration was measured in a 0.1 cm quartz cell, otherwise the band appeared at 35300 cm^{-1}. The spectrum given by Martin *et al.* might be apparently shifted due to some contamination of free bipyridine. As a matter of fact, free bipyridine shows a band at 35500 cm^{-1}.

We showed that low energy charge-transfer bands are observed when electrons are trapped by the central metal ion upon the reduction of a complex,

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1) E. König and S. Herzog, *J. Inorg. Nucl. Chem.*, **32**, 585, 601, 612 (1970).

2) Y. Kaizu, T. Yazaki, Y. Torii and H. Kobayashi, This Bulletin, **43**, 2068 (1970).

3) I. Fujita, T. Yazaki, Y. Torii and H. Kobayashi, *ibid.*, to be published.

4) G. M. Waind and B. Martin, *J. Inorg. Nucl. Chem.*, **8**, 551 (1958).

5) B. Martin, W. R. McWhinnie and G. M. Waind, *ibid.*, **23**, 207 (1961).

[*1] 4,4′-dimethyl- and 5,5′-dimethyl-2,2′-bipyridine are abbreviated to 4dmbip and 5dmbip, respectively.

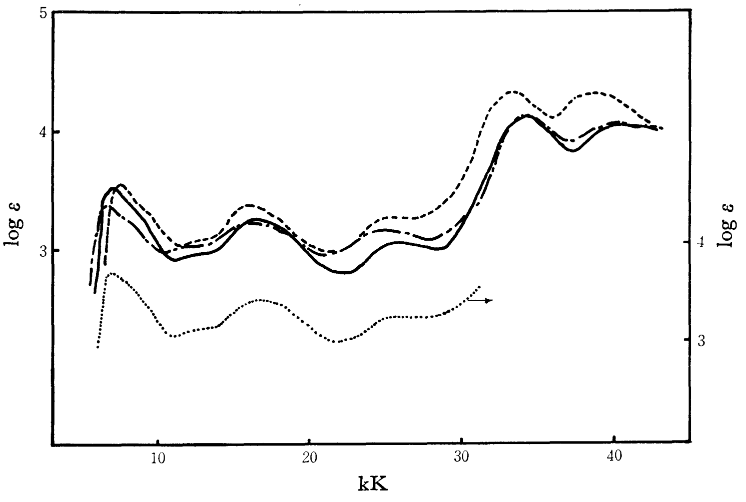

Fig. 1. Absorption spectra of the bipyridine complexes of cobalt(I) in methanol solution.
———: $[Co(bipy)_3]ClO_4$, — — —: $[Co\text{-}(4dmbip)_3]ClO_4$, - - - - -: $[Co(5dmbip)_3]ClO_4$, ·········: $Co(bipy)_2ClO_4$. The symbol (→) indicates the right ordinate.

while low energy (π,π^*) bands of the coordinating negative ion are observed when electrons are captured by the coordinating ligand.[2] Since we observed low energy charge-transfer bands, majority population of the electron furnished by reduction is concluded to localize at the central cobalt ion. The oxidation number of cobalt is +1. Since univalent cobalt has eight electrons in *d*-orbitals, two unpaired electrons are expected under the ligand field of D_3 symmetry. This is in good agreement with our observed magnetic moment 2.53 B.M.

In addition to tris(2,2′-bipyridine)cobalt(I) complex, it is well known that bis(2,2′-bipyridine)cobalt(I) complex exists.[6] The bis-complex shows an intense and diffuse spectrum very similar to that of the tris-complex. From the fact that tris(2,2′-bipyridine)nickel(II) complex, an isoelectronic system of tris(2,2′-bipyridine)cobalt(I) complex, gives rise to (d,d^*) transitions in the visible region, the low energy absorption band observed in the bis-complex has been assigned to (d,d^*) transitions by Császár.[7] We are convinced from our data that the bands in the near infrared and visible region should be assigned to 'metal to ligand' charge-transfer transitions.

Experimental

Tris(2,2′-bipyridine)- and bis(2,2′-bipyridine)cobalt(I) perchlorates were prepared by the same method as given in the literature.[4,6] Tris(4,4′-dimethyl-2,2′-bipyridine)- and tris(5,5′-dimethyl-2,2′-bipyridine)-cobalt(II) perchlorate were prepared by the same method with some modifications. The four compounds are deep blue. Tris(2,2′-bipyridine)cobalt(I) perchlorate we prepared showed a magnetic moment of 2.53 B.M. at room temperature. Waind and Martin, however, reported that the tris-complex was diamagnetic.[4,8] The bis-complex gave a moment of 2.71 B.M. The results of elemental analysis are shown in Table 1.

Table 1.

Complex	Analysis Co (%)	
	Calcd	Found
$[Co(bipy)_3]ClO_4$	9.4	9.7
$[Co(4dmbip)_3]ClO_4$	8.3	8.8
$[Co(5dmbip)_3]ClO_4$	8.3	8.5
$Co(bipy)_2ClO_4$	12.5	12.3

Measurement of the electronic absorption spectra of such air-sensitive compounds was described previously.[9] Spectra were measured using a Shimadzu automaticrecording spectrophotometer Model MPS-50.

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[6] A. A. Vlecek, *Nature*, **180**, 753 (1957).

[7] J. Császár, *Naturwissenschaften*, **46**, 488 (1959).

[8] B. Martin and G. M. Waind, *Proc. Chem. Soc.*, **1958**, 169.

[9] Y. Torii, T. Yazaki, Y. Kaizu, S. Murasato and H. Kobayashi, This Bulletin, **42**, 2264 (1969).