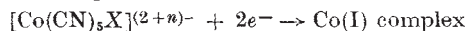


For the ions of azido-, thiosulphato-, nitro- and sulphonato-complexes:



The structure and the co-ordination number of the cobalt(I) complex are not known at present, though efforts are now being made to isolate the complex in a solid state from the solution.

NOBUFUMI MAKI
JUNNOSUKE FUJITA
RYUTARO TSUCHIDA

Laboratory of Inorganic Chemistry,
Faculty of Science,
Osaka University,
Kita-ku, Osaka.
Oct. 21.

¹ Pauling, L., "General Chemistry", 277 (1948).

² Maki, N., Shimura, Y., and Tsuchida, R., *Bull. Chem. Soc. Japan*, **30**, 909 (1957).

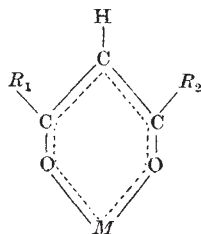
³ Vlček, A. A., *Nature*, **180**, 753 (1957).

Metal-Oxygen Stretching Frequencies in the Metal Chelate Compounds of β -Diketones

RECENTLY, many papers¹ have been published on the infra-red spectra of metal chelate compounds of β -diketones in the sodium chloride (4,000 ~ 650 cm^{-1}) region. The empirical assignments of the observed bands have also been made by Lecomte and other workers². Since the CO stretching bands can be identified without much ambiguity, attempts have been made to correlate their frequencies with the stability of the chelates³ or the ionization potential⁴ of various metals.

It is expected, however, that the metal-oxygen stretching frequencies of these compounds are chemically most interesting since they are closely related to the stabilities of the chelates. Unfortunately, they are difficult to identify because they appear outside the sodium chloride region, and, furthermore, strong coupling with other modes may be involved.

We measured the spectra of thirty-two compounds of the following type in the 1,700 ~ 280 cm^{-1} region using optical components of sodium chloride, potassium bromide and caesium bromide:



where, R_1 , R_2 and M are variables. It was found that, in acetylacetonates and benzoylacetonates, the bands, ranging from 420 to 480 cm^{-1} , shift to higher frequencies and increase in intensity as the metal is changed in the order (of stability): $\text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} < \text{Pd}^{2+}$, as is shown in Table 1.

Table 1

	Acetylacetonates	Benzoylacetonates
Co^{2+}	420 cm^{-1}	423 cm^{-1}
Ni^{2+}	453	452
Cu^{2+}	455	458
Pd^{2+}	465	478
Al^{3+}	490	470

Also, in Cu^{2+} or Ni^{2+} chelates of various β -diketones, the same band shifts to higher frequency as R_1 and R_2 are changed in the order (of stability): $\text{CF}_3 < \text{CF}_2 < \text{CF} < \text{CH}_3 < \text{CH}_2 < \text{C}_6\text{H}_5$, $\text{CH}_3 < \text{C}_6\text{H}_5$, as is shown in Table 2.

Table 2

R_1 , R_2	Cu^{2+}	Ni^{2+}
CF_3 , CF_3	445	427
CF_3 , CH_3	455	453
C_6H_5 , CH_3	458	453
C_6H_5 , C_6H_5	463	460

These results seem to suggest that this band may be due to one of the metal-oxygen stretching modes or is at least closely related to it. In order to confirm this and to determine the coupling nature of this band, the normal co-ordinate treatment is necessary and will be carried out.

We wish to thank Prof. R. C. Lord, jun., of the Massachusetts Institute of Technology, for aid in obtaining the spectra in the caesium-bromine region.

KAZUO NAKAMOTO
PAUL J. MCCARTHY
ARTHUR E. MARTELL

Department of Chemistry,
Clark University,
Worcester, Mass.
Nov. 5.

¹ Belford, R. L., Martell, A. E., and Calvin, M., *J. Inorg. Nuclear Chem.*, **2**, 11 (1956). Holtzclaw, jun., H. F., and Collman, J. P., *J. Amer. Chem. Soc.*, **79**, 3318 (1957). Dryder, R. P., and Winston, A., *J. Phys. Chem.*, **62**, 635 (1958).

² Lecomte, J., *Disc. Farad. Soc.*, **9**, 125 (1950). Duval, C., Freymann, R., and Lecomte, J., *Bull. Soc. Chim. France*, **19**, 106 (1952). Bratoz, S., Hadzi, D., and Rossmly, S., *Trans. Farad. Soc.*, **52**, 464 (1956). Mecke, R., and Funck, E., *Z. Electrochem.*, **60**, 1124 (1956). Bellamy, L. J., Spicer, G. S., and Strickland, J. D. H., *J. Chem. Soc.*, 4653 (1952).

³ Bellamy, L. J., and Branch, R. F., *J. Chem. Soc.*, 4487 and 4491 (1954).

⁴ West, R., and Riley, R., *J. Inorg. Nuclear Chem.*, **5**, 295 (1958).

Existence of Two Liquid Phases in the System Cobalt Chloride-Water-Acetone

Katzin and Ferraro¹ have examined the composition of the solid phases and their equilibrium solutions in the system cobalt chloride-water-acetone at 25° C. During further studies of solutions containing these components it has been noticed that for certain water-acetone mixtures the addition of cobalt chloride can lead to a separation of two liquid phases.

Fig. 1 gives the relation of the region of immiscibility to the phase diagram given in ref. 1. The results were obtained by titrating aqueous cobalt chloride solutions, made from the recrystallized 'Analar' hexahydrate, with 'Analar' acetone, weighing both the portion of aqueous solution and the final mixture with acetone. A few points were obtained by preparing saturated solutions of the salt in known water-acetone mixtures, and titrating these with acetone or with water-acetone mixtures. The points in the present work were obtained at room temperatures of 20-21° C., whereas the saturation curve was determined at 25° C. A tie-line running through the centre of the immiscible region is also included in the phase diagram. It was obtained by analysing the two phases for cobalt and for water (by a Karl Fisher titration).

The immiscible area follows the saturation curve fairly closely, but a number of experiments have shown that at 25° C. there is a single liquid phase