Investigations on Some Amine Complexes of Cobalt(II) Phthalimide. II. Infrared Spectroscopic Measurements

By Gopal NARAIN

(Received April 9, 1965)

The preparation of a series of amine complexes of cobalt(II) phthalimide and some preliminary investigations, such as their analysis and studies of their molecular weight and conductivity, have been reported in Part I.(1) It has there been pointed out that the non-electrolytic nature of the complexes shows that two phthalimide ions are co-ordinated along with the amine ligands, and that the co-ordination of the phthalimide ion to the metal can be either through the negatively-charged nitrogen or the oxygen of the carbonyl group. The present communication, related to infrared spectroscopic measurements, will attempt further to confirm and establish that both the amine and phthalimide ligands are co-ordinated to the cobalt atom.

Experimental

The spectra were obtained on a small infracord, using potassium bromide prisms.

---

1) G. Narain, P. Shukla and L. N. Srivastava, Communicated to *J. Prakt. Chem.* for publication.

TABLE. I. INFRAED ABSORPION BAND

	Name	
1	Cobalt(II) phthalimide	645w, 712s, 850w, 1055m, 1085w, 1140w, 1185w, 1310m, 1380s, 1465s, 1605m, 1725s, 1765m, 3140m.
2	Bi(phthalimido)-diaminocobalt(II)	680m, 715s, 860m, 1130w, 1225w, 1305m, 1385s, 1470s, 1610w, 1715w, 3260m.
3	Bi(phthalimido)-ethylenediaminocobalt(II)	675w, 712s, 850m, 935m, 975m, 1050s, 1130m, 1180s, 1210w, 1300m, 1380s, 1470s, 1610s, 1700s, 3240s.
4	Bi(phthalimido)-2, 2′-dipyridylcobalt(II)	650w, 680m, 720s, 750w, 765m, 850m, 1020w, 1060w, 1175s, 1300m, 1313w, 1375w, 1470s, 1600s, 1624s, 1710w.
5	Bi(phthalimido)-*o*-phenanthrolinecobalt(II)	650w, 680m, 725s, 750m, 855s, 870w, 960w, 1060w, 1105m, 1150m, 1230w, 1310w, 1360w, 1380s, 1430s, 1470s, 1500w, 1520m, 1575m, 1630m, 1714s.

Results

The spectra have been examined over the entire infrared range from 400—3500 cm^{-1}; the various bands obtained for individual complexes are listed in Table I.

Discussion

The examination of the spectra shows that there are two interesting regions, the NH and C:O stretching frequency regions.

As has been mentioned earlier, the phthalimide ion has the possibility of being coordinated to the metal atom either through the nitrogen or through the oxygen of the carbonyl group. The infrared spectra cannot make a sharp distinction between these two conditions, because any change in phthalimide nitrogen, which is directly linked to the carbonyl group, will alter the molecular environment and, accordingly, the frequency of the latter, even if it is not co-ordinated.[2] However, on the basis of the Lewis concept, it may be expected that the nitrogen, which is negatively-charged, will have better possibilities of being co-ordinated than the oxygen.[3] In the co-ordination through oxygen, steric hindrance will be effective, as is exemplified by the unsuccessful attempt to prepare some metal complexes with phthalimide as the ligand, complexes which would be analogous to acetamide complexes.[4]

All complexes (except those prepared by using 2, 2-′dipyridyl or *o*-phenanthroline as the ligand) show a single sharp absorption band in the vicinity of 3300 cm^{-1}; this is taken to be the NH-stretching frequency band. In free ammonia the band occurs at 3414 cm^{-1}. This negative shift of the frequency is a result of the co-ordination of the amine to the cobalt atom, thus resulting in the formation of a highly covalent M–N bond, which weakens the NH bond order. In the case of the ethylene diamine complex also, there is a considerable shift; this is again because of the co-ordination of the amine. In the case of 2, 2′-dipyridyl and *o*-phenanthroline complexes, there is no band in the above region. However, a comparison of the positions of the various bands with those of free ligands[5,6] shows that the frequencies are shifted to higher values in complexes, which clearly shows that the ligands are co-ordinated.[5]

The band observed in the carbonyl-stretching frequency region is of interest. In phthalimide, the band occurs at 1745 cm^{-1}, and in cobalt phthalimide it shifts to 1725 cm^{-1}, while in complexes it shifts to 1700—1710 cm^{-1}. The cause of this negative shift of frequency appears to be the electron density of nitrogen. In the case of cobalt(II) phthalimide, which is supposed to possess a partial covalent character, exhibited by its low solubility in polar solvents, the band shifts by only 25 cm^{-1}. This negative nitrogen has an orbital covalently bonding to the metal and an orbital perpendicular to the plane to the phthalimide. This filled orbital on nitrogen would help to direct a greater electron density towards the C=O bond; this would tend to increase the frequency. However, other factors, such as the ∝-mass effect and hydrogen bonding, tend to decrease the frequency; hence, an intermediate value is obtained. In the case of complexes, the direction of the added electron density reaches a saturation point, beyond which any added electron density tends to reduce the C=O double bond to a single bond and reduce the frequency. The addition of additional ligands to the cobalt(II) ion causes the metal ions to attempt to "back donate" into the available orbitals on the nitrogen of phthalimide. The filled orbital of the phthalimide nitrogen is made available by a quasiaromatic delocalisation. Thus, the following formulae would give a lower bond

---

2) S. Krimm, *J. Chem. Phys.*, **23**, 1371 (1955).

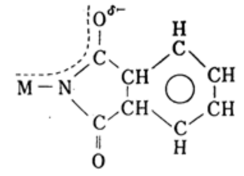
3) J. C. Bailar, "Chemistry of Co-ordination Compounds," New York (1956), p. 180.

4) W. Bagnall, M. Deane, S. Robinson and A. Steward, *J. Chem. Soc.*, **1961**, 1611.

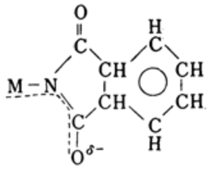
5) P. C. H. Mitchell, *J. Inorg. Nucl. Chem.*, **25**, 967 (1963).

6) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, **1962**, 4570.

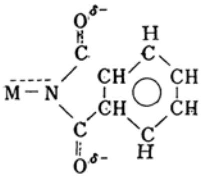
order to C=O and a lower frequency:



(I)



(II)



(III)

Another cause of the shift may be the ∝-mass effect.⁷⁾ In phthalimide, the nitrogen is linked to a very light hydrogen atom; hence, there is no hindrance in the normal motion of the CO group. In the case of complexes, the phthalimide nitrogen is linked to a heavy metal atom, which may cause a hindrance in its normal vibration, thus displacing the carbonyl frequency band to a lower value, although the magnitude of this shift would be small because, due to the cyclic nature of the ligand, the oxygen is vibrating against essentially the whole ligand. Hence, it appears that it is as a result of these factors that a negative shift of CO frequency is observed, although the oxygen of the carbonyl group is not co-ordinated.

Summary

Infrared measurements of a series of complexes prepared with cobalt(II) phthalimide and some amines of the [Co(Phthalimide)$_2$(amine)$_{2 or 1}$] type have been made. The spectra confirm that both phthalimide ions and amine molecules are co-ordinated; they further suggest that the co-ordination of phthalimide is through the nitrogen.

The author is thankful to Dr. J. V. Quagliano, Florida State University, Tallahasse, Florida, for his valuable suggestions in the theoretical interpretation of I. R. data; and to Dr. L. N. Srivastava and Dr. P. R. Shukla, Chemistry Department, Lucknow University, for their help in the preparation of the manuscript. He is also indebted to the Council of Scientific and Industrial Research for the award of a senior research fellowship for this work.

Department of Chemistry
Lucknow University
Lucknow, U.P., India,

---

7) G. F. Svatos, C. Kurran and J. V. Quagliano, *J. Am. Chem. Soc.*, **77**, 6159 (1955).