

Investigations on Some Amino Complexes of Copper(II) Phthalimide. II
Infra Red Absorption Spectroscopic Measurements

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Abstract

The I. R. measurements on a series of complexes, prepared with copper (II) phthalimide and aliphatic amines of type $[\text{Cu}(\text{amine})_2 \cdot (\text{Phthalimide})_2]^0$ have been done. The spectra indicate that the co-ordination of phthalimide ion to copper may be through the nitrogen and that the arrangement of two amine and two phthalimide ions around the copper atom may be trans planar.

Introduction

The preparation of a series of aliphatic amine complexes of copper phthalimide and some preliminary investigations such as their analysis molecular weight and conductivity, have been reported in Part I¹). It has been pointed out that the non-electrolytic nature of the complexes shows that two phthalimide ions are also co-ordinated along with the two amine ligand and that the co-ordination of phthalimide ion to the copper atom could be either through the negatively charged nitrogen or the oxygen of the carbonyl group. The present communication relates to the infra red spectroscopic measurements in order to further confirm that the phthalimide ions are coordinated to the metal.

Experimental

The infra red spectral measurements were carried out on an PERKIN-ELMER infra red spectrophotometer model 21 using a sodium chloride prism. The spectra were taken in nujol mulls.

Results

The spectra have been examined for the entire infra red range from 400—3500 cm^{-1} and the various bands obtained for individual complexes are listed in the following table.

¹) P. SHUKLA (Miss), M. P. KHARE and L. N. SRIVASTAVA, Communicated to Z. Prakt. Chem. for publication.

Table 1. Infra Red Bands

	Formulae	Infra Red Bands
1.	Phthalimide	645 w, 715 s, 792 w, 815 w, 1055 s, 1070 w, 1090 w, 1140 s, 1185 w, 1310 s, 1380 s, 1465 s, 1605 w, 1744 s, 1770 w, 3180 s
2.	Copper phthalimide	645 w, 712 s, 850 w, 1055 m, 1085 w, 1140 w, 1185 w, 1310 m, 1380 s, 1465 s, 1605 m, 1725 s, 1765 m, 3140 m
3.	Bipthalimido, bi(methylamino) copper (II)	675 m, 712 s, 740 m, 780 w, 855 m, 955 w, 1070 w, 1130 s, 1185 s, 1220 w, 1265 s, 1310 s, 1310 s, 1380 s, 1465 s, 1605 w, 1655 s, 3266 s
4.	Bipthalimido Bi(amino) copper (II)	670 m, 710 s, 855 w, 1075 m, 1130 s, 1185 m, 1225 m, 1290 s, 1315 s, 1380 s, 1460 s, 1510 w, 1525 m, 1545 m, 1560 m, 1610 m, 1655 s, 1715 s, 3270 m
5.	Bipthalimido bi(ethylamino) copper (II)	675 s, 720 s, 850 m, 1055 m, 1075 s, 1130 s, 1180 s, 1285 m, 1310 s, 1380 s, 1460 s, 1303 s, 1650 s, 1720 m, 3280 s
6.	Bipthalimido, bi(n-propylamino) copper (II)	675 m, 720 m, 850 w, 1050 w, 1130 m, 1180 m, 1310 m, 1380 w, 1465 s, 1545 m, 1610 m, 1645 s, 3280 w
7.	Bipthalimido bi(iso-propylamino) copper (II)	670 m, 722 s, 855 m, 1055 w, 1075 m, 1107 m, 1180 m, 1210 w, 1295 w, 1310 m, 1380 m, 1465 s, 1605 m, 1640 s, 1715 m, 3285 s
8.	Bipthalimido bi(butylamino) copper (II)	670 m, 725 m, 850 w, 1130 m, 1180 m, 1315 m, 1380 s, 1460 s, 1510 w, 1520 w, 1560 w, 1580 w, 1650 s, 1685 m, 3290 m
9.	Bipthalimido bi(amyamino) copper (II)	675 w, 725 s, 775 w, 850 m, 955 w, 1075 w, 1100 w, 1135 s, 1185 s, 1210 s, 1310 s, 1380 s, 1463 s, 1550 w, 1610 m, 1640 s, 3302 s
10.	Bipthalimido bi(diethylamino) copper (II)	670 m, 715 s, 740 m, 780 m, 860 m, 960 w, 1075 s, 1090 s, 1140 w, 1185 m, 1220 w, 1295 w, 1305 s, 1380 m, 1460 s, 1500 w, 1645 s, 3310 s
11.	Bipthalimido bi(di-propylamino) copper (II)	675 m, 710 s, 740 m, 825 w, 855 s, 950 m, 1050 m, 1090 w, 1125 s, 1180 s, 1225 w, 1265 w, 1310 s, 1375 s, 1460 s, 1605 m, 1650 s, 1715 m, 3160 w, 3300 m
12.	Bipthalimido, bi(di-butylamino) copper (II)	675 w, 710 s, 745 w, 855 m, 1050 m, 1065 w, 1080 w, 1130 s, 1185 s, 1265 m, 1290 w, 1310 m, 1380 s, 1460 s, 1605 s, 1710 w, 3370 s

Discussion

The position of the various bands have been assigned by analogy to the spectra of other known amine complexes. The examination of the spectra shows them to be exactly similar to one another and to free phthalimide with a few differences in NH and C:O stretching frequency regions.

As has been mentioned earlier the phthalimide ion has the possibility of being co-ordinated to the metal atom, either through the nitrogen or through the oxygen of the carbonyl group. The IR spectra cannot make a sharp distinction between the two conditions because any change in the phthalimide nitrogen which is directly linked to the carbonyl group, will alter the molecular environment and accordingly the frequency of latter even if it is not co-ordinated²⁾. But on the basis of LEWIS concept it is expected that the nitrogen which has the negative charge, has better possibilities of being co-ordinated³⁾, than the oxygen. Also if co-ordination is to be through oxygen, each phthalimide ion will occupy two co-ordination position and hence steric hindrance will be effective, which is exemplified by the unsuccessful attempts of preparing some metal complexes with phthalimide as ligand, analogous to acetamide complexes⁴⁾. Moreover in the structural interpretation of some copper succinimide amine complexes by WERNER⁵⁾, the co-ordination was predicted through the negative nitrogen. It is thus suggested that in this case also the co-ordination is most probably taking through the nitrogen.

All complexes show a single sharp absorption band in the vicinity of 3300 cm^{-1} , which is assigned to be the NH stretching frequency band. In free ammonia the band occurs at 3414 cm^{-1} . This negative shift of the frequency is because of the co-ordination of the amine to the copper atom, thus resulting in the formation of a highly covalent M—N bond, which weakens the NH bond order. The magnitude of this negative shift in these complexes decreases as the molecular weight of amine increases, which indicates that the covalency of M—N bond and the stability of the complexes decreases as the molecular weight of the amine increases⁶⁾. The ammonia complex is thus stablest of all with a shift of about 140 cm^{-1} while the di-n-butylamine complex is least stable with a shift of only 50 cm^{-1} .

²⁾ S. KRIMM, *J. chem. Physics* **23**, 1371 (1955).

³⁾ J. C. BAILAR, *Chemistry of Co-ordination compounds* (Rheinhold Publishing Corporation New York) 1956, p. 180.

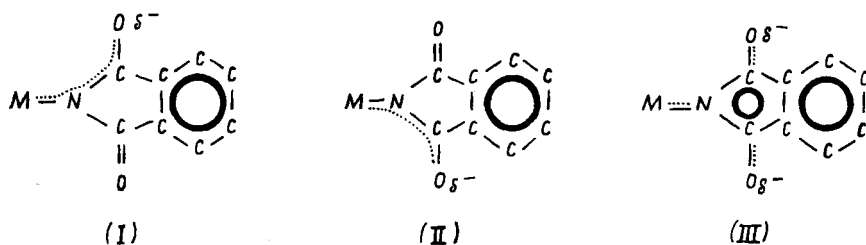
⁴⁾ W. BAGNALL, M. DEANE, S. ROBINSON and A. STEWART, *J. chem. Soc. [London]* 1611 (1961).

⁵⁾ LEY and WERNEY, *Ber. dtsch. chem. Ges.* **40**, 705 (1905).

⁶⁾ K. NAKAMOTO, *Infra red spectra of Inorganic and Co-ordination compounds* (John Wiley & Sons New York, London) 1963, p. 145.

The presence of a single sharp band in the above region also shows the complexes to be trans planar⁷⁾, as the coupling of two trans N—M bonds gives a symmetric and antisymmetric vibration, of which only the latter is infra red active. A cis complex on the other hand should give a doublet in the above region.

The band observed in the carbonyl stretching frequency region is of interest. In phthalimide, the band occurs at 1745 cm^{-1} , in copper phthalimide it shifts to 1725 cm^{-1} while in complexes it shifts further to 1655 cm^{-1} . The cause of this negative shift of the frequency appears to be the high electron density at nitrogen. In case of copper phthalimide, which is supposed to possess a partial covalent character, exhibited in its low solubility in polar solvents, the band shifts only by 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 direct greater electron density towards the $>\text{C}=\text{O}$ bond and this tends to increase the frequency, But other factors such as α , mass affect and hydrogen bonding (discussed below) tend to decrease the frequency and hence an intermediate value is obtained. In case of complexes the direction of the added electron density reaches a saturation point beyond which this added electron density tends to reduce the $>\text{C}=\text{O}$ double bond to a single bond and reduce the frequency. The addition of additional ligands to copper (ii) ion causes the metal ions to attempt to "back donate" into available orbitals on the nitrogen of phthalimide. The filled orbital of the phthalimide nitrogen is made available by a quasi-aromatic delocalization. Thus formulae as follow would give a lower bond order to $\text{C}=\text{O}$ and a lower frequency.

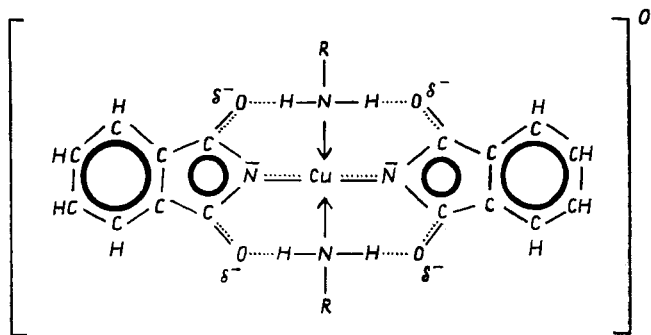


Another cause of this shift may be α -mass effect⁸⁾. In phthalimide the nitrogen is linked to a very light hydrogen atom and hence there is no hindrance in the normal motion of CO group. In case of complexes the phthalimide nitrogen is linked to a heavy metal atom which may cause a hindrance in the normal vibration of the carbonyl group, which displaces the carbonyl frequency band to a lower value, although the magnitude of the shift would

⁷⁾ C. F. SVATOS, C. CURRAN and J. V. QUAGLIANO, *J. Amer. chem. Soc.* **77**, 6159 (1955).

⁸⁾ R. N. JOHNS, W. E. FARBER and W. A. MUELLER, *Canad. J. Chem.* **35**, 504 (1957)

be little, because due to the cyclic nature of the ligand the oxygen is vibrating against essentially the whole ligand. Hydrogen bonding may also be a cause of this decreased frequency but as there is no possibility of hydrogen bonding in case of copper phthalimide it is not the only factor responsible for the shift. However in case of the complexes, the hydrogen of the amine may be considered to be forming a weak intermolecular hydrogen bond with the carbonyl oxygen. As a result of the combined effects of these factors it appears that the carbonyl frequency is being shifted to a lower value although the oxygen of the carbonyl group is not coordinated to the copper atom. The structure of the complexes may then be represented as:



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