Copper(II) Complexes of 4-Substituted N,N-Dimethylbenzamides

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Introduction

Elucidation and characterization of the mode of bonding of amides to transition metals continues to be of interest [1–10]. This paper describes a hitherto unreported synthesis of a series of copper benzamides in an effort to learn more about characterizing their bonding. The ligands were 4-substituted-N,N-dimethylbenzamides with H, CH_3, Cl, Br, F, NO_2, and CH_3O as the substituents. The stoichiometry of each complex corresponded to $Cu\{4\text{-}X\text{-}C_6H_4CON(CH_3)_2\}_4(ClO_4)_2$. N,N-dimethylbenzamides were used in order to force coordination to oxygen due to the severe steric hindrance around the nitrogen which molecular models show prevent coordination of four ligands through the nitrogen. The ring substituents were varied in order to see if they would affect measured parameters of both the ligands and the complexes. Since the ring is conjugated to the carbonyl group and not the amide nitrogen, substituent effects or lack of them could be helpful in characterizing oxygen or nitrogen bonding.

Experimental

Synthesis

The benzamides were prepared following the procedures of Pinchas *et al.* [11] by bubbling N,N-dimethylamine into a solution of dry ethyl ether and the 4-substituted benzoyl chloride. For those compounds which had been previously synthesized, the melting points agreed with the literature values. The copper complexes were prepared following a modification of the procedure of Madan and Denk [12]. Hydrous copper(II) perchlorate was dehydrated by stirring at 30 °C with a 50% mol excess of 2,2-dimethoxypropane until the solution turned emerald green. A weight of the benzamide equal to a 4:1 mol ratio to copper was dissolved in a minimum amount of anhydrous ethanol and added to the dehydrated copper perchlorate. An equal volume of ether was added and the solution cooled in an ice bath. If precipitation did not take place, more 2,2-dimethoxy propane was added, the solution heated and evaporated to 10 ml. The solution was cooled along with the addition of ether. The copper complexes of 4-bromo-N,N-dimethylbenzamide and 4-methoxy-N,N-dimethylbenzamide required cooling to liquid nitrogen temperatures before precipitating out.

The copper content of each complex was determined by EDTA titration. Carbon, hydrogen and nitrogen analyses were performed by the Galbraith Laboratories.

Physical Measurements

Infrared spectra of all complexes and free ligands were obtained as KBr pellets using a Perkin Elmer Model 21 spectrophotometer. Magnet moments were obtained from magnetic susceptibility measurements from 70 K to room temperature using the Gouy technique. A Varian 3-inch magnet and regulated power supply was used. $Hg\{CO(SCN)_4\}$ was used as a calibrant. Conductance measurements were made using a Beckman Model RC-18A conductivity bridge. Measurements were made at 25 °C in nitromethane on 0.01 *M* solutions. Electron spin resonance measurements were made using a spectrometer modeled after a standard Varian spectrometer. A Varian low noise 12-inch magnet, Varian dual sample, X-band rectangular cavity, a Philco low noise detector crystal and Princeton Applied Research electronics were used.

Results and Discussion

Synthesis and Structure

Synthesis of those ligands previously not prepared proceded smoothly to yield colorless platelets or needles of the material. The reaction between the various ligands and anhydrous copper perchlorate, described in the experimental section, yielded well defined crystalline powders. As noted, some of the complexes required cooling to liquid nitrogen temperatures before precipitation. The complexes are all colored some shade of blue and were all slightly hydroscopic. Table I gives the appearance of the complexes and shows the results of the elemental analysis of the complexes which confirms the 4:1 ligand to copper stoichiometry. Table II gives specific conductance data, the magnetic moments, infrared amide I band frequencies and esr anisotropic g values for the complexes. The magnetic moments are within the expected range for copper(II) complexes and are consistent with both an octahedral or tetragonal field [13]. The conductance data suggest the presence of 1:2 electrolytes for all complexes [9, 15, 16]. The

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TABLE I. Analytical Data.

Compound	Appearance	Elemental Analysis							
		Cu		C		H		N	
		Theo.	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.	Exp.
$Cu[C_6H_5CON(CH_3)_2]_4(ClO_4)_2$	light grey blue	7.40	7.57	50.31	50.31	5.12	5.21	6.52	6.19
$Cu[pCH_3C_6H_4CON(CH_3)_2]_4(ClO_4)_2$	marine blue	6.95	6.95	52.47	51.74	5.68	5.56	6.12	5.68
$Cu[pFC_6H_4CON(CH_3)_2]_4(ClO_4)_2$	dark blue	6.83	6.95	46.41	46.30	4.30	4.60	6.02	5.93
$Cu[pClC_6H_4CON(CH_3)_2]_4(ClO_4)_2$	medium sky blue	6.38	6.52	43.35	42.90	4.01	4.11	6.52	6.25
$Cu[pBrC_6H_4CON(CH_3)_2]_4(ClO_4)_2$	light sky blue	5.41	5.38	36.79	36.67	3.41	3.67	4.77	4.71
$Cu[pNO_2C_6H_4CON(CH_3)_2]_4(ClO_4)_2$	grey blue	6.12	6.07	41.58	41.43	3.85	4.16	10.78	10.59
$Cu[pCH_3OC_6H_4CON(CH_3)_2]_4(ClO_4)_2$	blue green	6.49	6.60	49.04	49.32	5.31	5.40	5.72	5.55

TABLE II. Conductance, Magnetic, Infrared and ESR Data.

Compound	Λ, ohm^{-1}	Amide I Frequency, cm^{-1}		μ_{eff}, B.M.	$g_z(g_{\parallel})$	$g_y(g_\perp)$	$g_x(g_\perp)$
		Free Ligand	Complex				
$Cu\{C_6H_5CON(CH_3)_2\}_4(ClO_4)_2$	165.2	1627	1632	1.97	2.403	2.064	2.140
$Cu\{pCH_3C_6H_4CON(CH_3)_2\}_4(ClO_4)_2$	161.9	1618	1632	1.93	2.347	2.061	2.139
$Cu\{pFC_6H_4CON(CH_3)_2\}_4(ClO_4)_2$	150.7	1625	1633	1.98	2.393	2.058	2.140
$Cu\{pClC_6H_4CON(CH_3)_2\}_4(ClO_4)_2$	151.9	1629	1631	2.02	2.400	2.061	2.137
$Cu\{pBrC_6H_4CON(CH_3)_2\}_4(ClO_4)_2$	148.3	1624	1632	2.03	2.397	2.062	2.138
$Cu\{pNO_2C_6H_4CON(CH_3)_2\}_4(ClO_4)_2$	122.2	1638	1638	1.94	2.383	2.050	2.138
$Cu\{pCH_3OC_6H_4CON(CH_3)_2\}_4(ClO_4)_2$	150.6	1616	1630	1.94	2.396	2.064	2.139

perchlorate ion is not bound to the inner coordination sphere. The value for the 4-nitro complex is somewhat lower than the others and may indicate a weaker bond between copper and the 4-nitro benzamide so that perchlorate can compete for a coordination site. This effect has been observed for the 4-nitroacetanilide complex of nickel perchlorate [9].

Mode of Bonding

Many studies have attempted to assign a shift in the amide I bond to lower frequencies upon complexation as evidence for coordination through the oxygen [1, 3–5, 7–10]. Conversely, a shift to higher frequencies upon complexation was taken to mean coordination to the amide nitrogen. One study [10], however, has indicated that the direction of frequency shifts may not always indicate the same type of bonding. Since some protonated amide complexes are thought to bond through the nitrogen [14–16], question as to the validity of this criteria still remains. The problem is a lack of an independent means of characterizing the site of bonding.

The ligands used in this study all have two N-methyl groups which provide considerable steric hindrance to coordination through the amide nitrogen. Indeed, molecular models show that in order to achieve the stoichiometry seen in this study, $ML_4(ClO_4)_2$, it is impossible for coordination to occur through the nitrogen. Previous studies have been carried out using, N,N-dimethylformamide as a ligand [10], however, the stoichiometry has been no higher than 1:2. Molecular models show that in those cases either nitrogen or oxygen coordination could easily occur. Support for oxygen coordination in the present study may be found from esr measurements taken on the complexes. Nitrogen donor ligands usually yield $g_{\parallel}$ values between 2.20–2.30 and $g_\perp$ values between 2.04–2.06, whereas oxygen donor ligands show $g_{\parallel}$ between 2.35–2.45 and $g_\perp$ between 2.06–2.09 [17]. A study involving distorted octahedral CuA_6 amide complexes was characterized as oxygen bonded using this criteria [17]. The esr data in the present study, shown in Table II, indicate a rhombic field yielding g_x, g_y and g_z values. The g_z values correspond to $g_{\parallel}$ and one of the two $g_\perp$ values of 2.35–2.403 and 2.056–2.064 respectively and would thus support coordination through the oxygen.
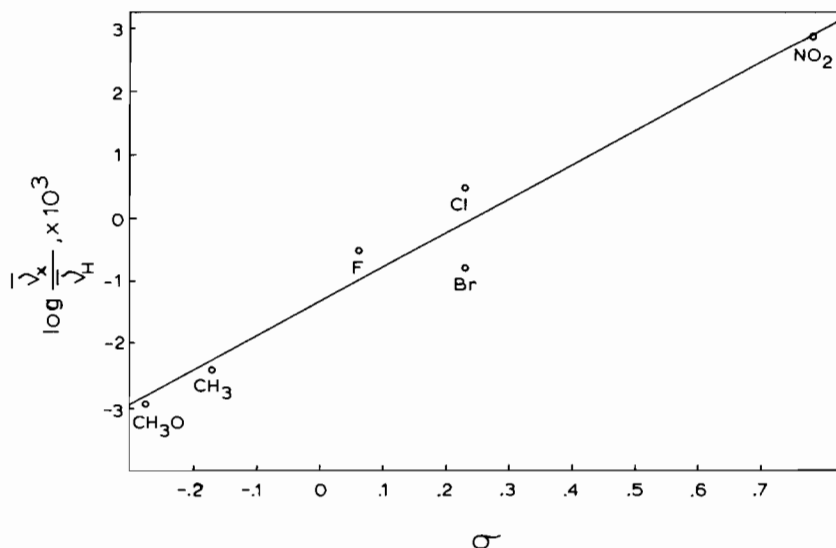
Fig. 1. Hammet plot of free ligand amide I bond frequency dependence upon substituent using Hammet σ values. Unsubstituted N,N-dimethylbenzamide was used as the reference compound.

Infrared Amide I Frequencies

Having established the point of coordination independent of IR measurements, the infrared amide I bond frequencies shown in Table II may now be examined. The values are seen to increase upon complexation, rather than decrease as is usually the case with oxygen coordination. Thus the widely used general rule that a decrease in the amide I frequency upon complexation means oxygen coordination is not applicable here and may not apply to other situations without independent confirmation of the mode of bonding. Further, the amide I bond of the free ligand shows a characteristic value for each substituent in the series. Yet the same bond for the complexes occurs at virtually the same frequency. It was possible to correlate the free ligand amide I bond frequency dependence upon substituent with Hammet σ values as shown in Fig. 1. The reference compound was chosen to be N,N-dimethylbenzamide. It is interesting to note that no correlation was found in a previous study of substituted benzamides [9]. The values in Table II, however, show that no correlation is possible for the complexes. Disappearance of the substituent effect upon complexation provides further evidence of coordination to the oxygen. If coordination through the nitrogen occurred, the substituent effect seen in the free ligand amide I frequencies should occur in the complexes as well because the electron environment around the oxygen would be essentially unaltered. Coordination of the carbonyl oxygen to a metal would override small substituent effects and cause all amide I frequencies to occur at the same value.

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