

II. CHEMISTRY

Coordination Compounds

MORPHOLINE COMPLEXES OF COPPER(II) ARYL CARBOXYLATES

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Adducts of Copper(II) aryl carboxylates with morpholine were prepared by interacting the reactants in 1 : 1 molar ratio or using a large excess of morpholine in acetone medium. Analytical results show that the adducts are either mono-morpholine or bis-morpholine complexes of 1 : 1 or 1 : 2 stoichiometry formulated as $\text{Cu}(\text{O}_2\text{CC}_6\text{H}_4\text{R})_2(\text{Morph})_n$ where R is H, CH_3 -*o*, CH_3 -*m*, Cl-*o*, Cl-*m*, Br-*o*, CH_3 O-*o*, CH_3 O-*m*, CH_3 O-*p*, NO_2 -*o*, NO_2 -*m*, NO_2 -*p*, OH-*o*, OH-*m*, and OCOCH_3 -*o*; Morph is Morpholine and *n* is 1 or 2. Conductance measurements show that all these adducts are non-ionic. Magnetic and electronic spectral studies suggest that mono-morpholine adducts are dinuclear syn-syn carboxylate bridged species whilst bis-morpholine adducts are mononuclear distorted octahedral molecules. Infrared spectra show that morpholine behaves as a N-bonded monodentate ligand.

Keywords: Copper(II) Aryl Carboxylates; Morpholine Adducts.

INTRODUCTION

A variety of copper(II) aryl carboxylates and their adducts with various nitrogen bases have been prepared and studied with a view to investigate their structure and magnetic properties (Lewis & Thompson, 1963; Lewis & Mabbs, 1965; Lewis *et al.*, 1965, 1969; Kato *et al.*, 1964; Jotham *et al.*, 1972; and Ablov *et al.*, 1969). All these carboxylates are dimeric, syn-syn carboxylate bridged species of sub-normal magnetic moments which generally give rise to 1 : 1 dimeric, syn-syn carboxylate bridged adducts with donor molecules irrespective of the nature of carboxylate group and the donor ligand. Since no such adducts of morpholine with copper(II) aryl carboxylates have been reported in literature, we undertook the preparation and characterization of adducts of morpholine with copper (II) aryl carboxylates with a view to see whether it forms usual mono-morpholine dimeric adducts of 1 : 1 or monomeric bis-morpholine adducts of 1 : 2 stoichiometry.

MATERIALS AND METHODS

Copper (II) aryl carboxylates were prepared by standard published methods (Lewis & Mabbs, 1965). Morpholine (BDH) was purified by fractional distillation and stored over KOH pellets. Solvents were purified by conventional methods.

Copper was estimated gravimetrically as cuprous thiocyanate $\text{Cu}_2(\text{SCN})_2$. C and H contents of the complexes were determined. The N contents of a few samples were also determined. Conductance measurements on 10^{-3} M complex solutions in MeOH and PhNO_2 were made with Toshniwal Conductivity Bridge Type CL01/02. Molecular weights were determined cryoscopically in PhNO_2 . Magnetic

moments were measured by Gouy's method. Electronic spectra were recorded on Carl Zeiss UV VIS Spectrophotometer while diffuse reflectance spectra were recorded on UV VIS Spectrophotometer Type SP 700 A. Infrared spectra were recorded in the range 4000–200 cm^{-1} on Perkin Elmer 621 Grating Double Beam Spectrophotometer.

Preparation of Adducts

All the adducts discussed in this communication were prepared by the same procedure as reported earlier (Kumar *et al.*, 1975) except copper(II) *o*-bromobenzoate adduct which is prepared by the interaction of morpholine with copper(II) *o*-bromobenzoate generated *in situ*.

Bis(o-bromobenzoate) morpholine copper(II):

Copper(II) *o*-bromobenzoate was generated in solution by refluxing basic copper carbonate (2.86g; 12 millimole) with *o*-bromobenzoic acid (8.04g; 40 millimole) in ethanol (150 ml) for fourteen hours and filtering off excess of the unreacted basic copper carbonate. One equivalent of morpholine (1.74g; 20 millimole) was added to the filtrate. The reaction mixture was concentrated and set aside for crystallization for 24 hours. A green crystalline product of formula $\text{Cu}(\text{O}_2\text{CC}_6\text{H}_4\text{Br-}o)_2(\text{C}_4\text{H}_9\text{ON})$ was obtained. It was filtered, washed with acetone, dried in air and finally under vacuum over P_2O_5 at 60°.

The analytical data of the adducts prepared are presented in Table I. Molecular weight, conductance, magnetic moments and electronic spectra are cited in Table II. Important bands in their infrared spectra are given in Table III.

RESULTS AND DISCUSSION

All of the adducts isolated are crystalline solids, quite stable in air except *m*-chlorobenzoate and *p*-methoxybenzoate adducts, which decompose on prolonged standing even under anhydrous conditions. The adducts are soluble in common organic solvents like methanol, ethanol, acetone, benzene and nitrobenzene except *m*- and *p*-nitrobenzoate adducts which are insoluble in all these solvents. The adducts have been assigned a general formula $\text{Cu}(\text{O}_2\text{CC}_6\text{H}_4\text{R})_2(\text{Morph})_n$ ($n=1$ when $\text{R}=\text{CH}_3$ -*o*, CH_3 -*m*, $\text{Br-}o$, OCOCH_3 and $n=2$ when $\text{R}=\text{H}$, $\text{Cl-}o$, $\text{Cl-}m$, NO_2 -*o*, NO_2 -*m*, NO_2 -*p*, $\text{CH}_3\text{O-}o$, $\text{CH}_3\text{O-}m$, $\text{CH}_3\text{O-}p$, $\text{OH-}o$ and $\text{OH-}m$). Conductance values in methanol and nitrobenzene are in the range 15.8–43.8 and 0.04–0.23 $\text{mole}^{-1} \text{ohm}^{-1} \text{cm}^2$ (Table II) respectively which are far below than the values of 120–140 and 20–40 $\text{mole}^{-1} \text{ohm}^{-1} \text{cm}^2$ reported for uni-uni valent electrolytes in methanol and nitrobenzene respectively (Carty, 1967; and Lever, 1965). These values suggest that the adducts are non-ionic in methanol and nitrobenzene. Molecular weight studies were carried on a few samples only (Table II); others were either insufficiently soluble or insoluble in benzene and nitrobenzene. These investigations show that 1 : 1 adducts are dimeric whereas 1 : 2 adducts are monomeric.

Magnetic Moments

The magnetic moment values of 1 : 1 dimeric complexes fall in 1.40–1.55 B. M. range at room temperature (Table II) which are lower than the spin magnetic

TABLE II
Molecular weights, molar conductance, magnetic and electronic spectral data of complexes of copper (II) aryl carboxylates

Complex*	Molecular Weight Found	Calcd.**	Molar Conductance Mole ⁻¹ In MeOH	ohm ⁻¹ cm ² In PhNO ₂	Magnetic μ _{eff} B. M.	Moments Temp. °K	Electronic Band I (cm ⁻¹)	Spectral Data Band II (cm ⁻¹)
1 : 1 Complexes								
1.	804	420	32.3	0.17	1.40	296	14240 ^a 13790 ^b 13840 ^c	25770 ^a sh 24940 ^b sh —
2.	866	420	27.4	0.11	1.42	296	13990 ^a 13960 ^b 13820 ^c	24240 ^a sh 25310 ^b sh —
3.	—	550	39.2	0.13	1.55	294	14080 ^a 14840 ^c	25030 ^a sh —
4.	—	508	39.4	—	1.40	295	15250 ^c	—
1 : 2 Complexes								
5.	453	480	38.4	0.04	2.08	293	13460 ^c 13260 ^a	— —
6.	—	549	43.2	—	1.96	293	13820 ^c	—
7.	600	549	35.3	0.11	1.93	294	13550 ^c 14020 ^a	— —
8.	—	570	40.9	—	1.98	295	13860 ^c	—
9.	—	570	—	—	2.07	293	14590 ^a	—
10.	—	570	—	—	1.90	295	14810 ^b	—
11.	—	540	43.8	0.11	1.90	295	13240 ^b	—
12.	512	540	32.6	0.05	1.89	294	13820 ^c	—
13.	522	540	15.8	0.07	1.93	297	13440 ^c	—
14.	—	512	38.7	0.07	2.01	295	13890 ^c	—
15.	—	512	31.5	0.23	1.97	295	13920 ^c	—

*Number refers to the complex in Table I.

**Calculated for monomeric formula weight.

a: In benzene; b: Diffuse reflectance spectra; c: in methanol.

moment value of 1.73 B. M. for copper(II) ion, but are quite similar to the values of magnetic moments observed ~1.5 B. M. in so many other dimeric copper(II) carboxylates and their 1 : 1 adducts (Kato *et al.*, 1964). However, there is a possibility that those adducts whose molecular weight could not be determined may be polymeric in nature. But this possibility is ruled out as magnetic moments observed for polymeric adducts are still lower than the values reported for dimeric complexes ~ 1.5 B. M. (Kato *et al.*, 1964). Moreover polymeric complexes are generally insoluble in nature. But adducts isolated herein are quite soluble in one or the other organic solvent. This suggests that all those adducts whose molecular weight could not be determined are also dimeric in nature. These observations suggest that mono-morpholine adducts are dimeric and possess a syn-syn carboxylate bridged structure similar to copper(II) acetate monohydrate (Figgis & Martin, 1956).

The magnetic moment values of monomeric bis-morpholine adducts fall in the range 1.89–2.08 B. M. (Table II) suggesting that these complexes possess a distorted octahedral structure analogous to those of the structure of magnetically dilute, 6-coordinated complexes of copper (II) (Kato *et al.*, 1964).

Electronic Spectra

1 : 1 adducts show two bands (I and II) in the regions 13,000–15,000 and 24,000–28,000 cm^{-1} respectively. Band I appears as a broad band and originates from copper(II) ion under the influence of octahedrally oriented ligands and is assigned to $d_{zz}, d_{yz} \rightarrow d_{x^2-y^2}$ transition (Dubicki *et al.*, 1966). Band II which is closely related with Cu-Cu linkage appears as a shoulder analogous to 1 : 1 dimeric carboxylate bridged complexes of copper(II) (Kokot & Martin, 1964; and Hibdon & Nelson, 1973) and has been assigned to $d_{xy} \rightarrow d_{x^2-y^2}$ transition. The electronic spectra of 1 : 1 adducts in methanol invariably show only band I $\sim 13,000 \text{ cm}^{-1}$ indicating that these species possess a different structure in solution from the solid phase and may have a monomeric octahedral structure due to solvent coordination (Nasanen & Melnik, 1969).

The electronic spectra of 1 : 2 adducts invariably show one broad band centred $\sim 14,000 \text{ cm}^{-1}$ which is quite similar to band I of 1 : 1 adducts and to the band generally observed in magnetically dilute octahedral complexes of copper(II) (Dubicki *et al.*, 1966) suggesting that bis-morpholine adducts also possess a distorted octahedral configuration.

Infrared Spectra

In liquid morpholine NH stretching vibration occurs at 3340 cm^{-1} whereas in the adducts this frequency is shifted to lower frequencies $3261\text{--}3110 \text{ cm}^{-1}$ (Table III). This indicates that morpholine coordinates through its nitrogen atom. The COC stretching frequency of morpholine shows a slight positive shift of $4\text{--}20 \text{ cm}^{-1}$ in the adducts which corroborates the conclusion that morpholine coordinates through its nitrogen atom. Two strong bands around 1600 and 1400 cm^{-1} are also observed in the infrared spectra of the adducts which have been assigned to assymmetric and symmetric COO stretching vibrations respectively. These bands are composite in nature and have some additional weak bands or shoulders associated with them. No definite conclusions can be drawn from these bands although these bands have been frequently used in the past literature to ascertain the nature of bonding of the carboxylate groups in these systems (Cotton *et al.*, 1973). Compared with the infrared spectra of the morpholine and uncomplexed copper(II) carboxylates, these complexes show some additional bands in the regions $420\text{--}550$ and $350\text{--}310 \text{ cm}^{-1}$. These have been tentatively assigned to CuO and CuN stretching vibrations as reported for the complexes of morpholine with transition metal halides and other salts (Ahuja, 1969).

All these investigations corroborate the findings of magnetic and spectral studies which show 1 : 1 adducts to be dimeric containing syn-syn bridging carboxylate groups and 1 : 2 adducts as monomeric, 6-coordinated molecules of distorted octahedral configuration in which carboxylate groups behave as bidentate chelating ligands.

TABLE III
Infrared spectral data (cm^{-1}) of morpholine complexes of copper (II) aryl carboxylates

Complex*	νNH	$\text{A}_{\text{sym.}}\nu\text{COO}$	$\text{Sym.}\nu\text{COC}$	νCuO	νCuN
$\text{C}_6\text{H}_5\text{ON}$	3340s	—	—	1095s	—
1 : 1 Complexes					
1.	3212m	1618s	1400m	1109s	362m, 337w, 321m
2.	3261m	1622s	1398m	1115s	389w, 358m, 326m
3.	3110m	1614s	1593s	1102s	317m, 326m
4.	3168m	1632s	1414m	1107s	420sh, 382w, 332m, 326m
1 : 2 Complexes					
5.	3190m	1602s	1398s	1112s	398m, 349s
6.	3122w	1603s	1389w	1106s	372m, 351m, 317s
7.	3199m	1608s	1417m	1112s	352s, 336s, 312s
8.	3184m	1616s	1402m	1111s	401m, 392s, 337s
9.	3216m	1601s	1392s	1099s	398sh, 362m, 349m
10.	3225m	1614s	1404m	1110s	382m, 348s
11.	3110m	1605s	1400m	1110s	362m, 339m
12.	3202m	1602s	1398m	1102s	418w, 380s, 352s
13.	3215s	1600s	1403s	1109s	406m, 341s
14.	3255m	1602s	1408s	1112s	382w, 353s
15.	3174m	1601s	1399s	1103s	376m, 336s

*Number refers to the complex in Table I.

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