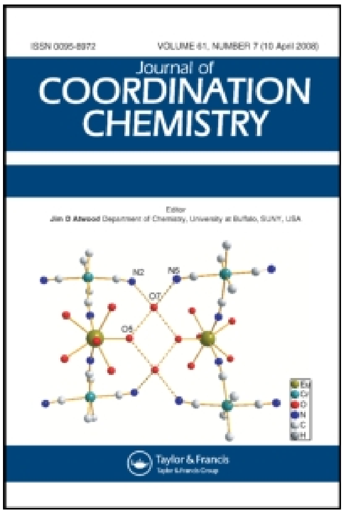

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Edmund Kwiatkowski[a]; Urszula Dettlaff-weglikowska[a]
[a] Institute of Chemistry, University of Gdansk, Gdansk, Poland

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ADDUCTS OF BIS[1,1,1-TRIFLUORO-4-PHENYLBUTA-2,4-DIONATO]COPPER(II) AND DERIVATIVES

EDMUND KWIATKOWSKI and URSZULA DETTLAFF-WEGLIKOWSKA

Institute of Chemistry, University of Gdańsk, ul. Sobieskiego 18, 80-952 Gdańsk, Poland

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Over 80 adducts of bis[1,1,1-trifluoro-4-phenylbuta-2,4-dionato]copper(II) and of its derivatives containing various substituents attached in the *para* position of the phenyl ring with the donors 1,4-dioxane, 1,3-dioxane, tetrahydrofuran, pyrazine, morpholine, 1,4-diazabicyclo-(2,2,2)-octane, pyridine, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 3,4-dimethylpyridine and 3,5-dimethylpyridine have been synthesized and characterized. Most of them contain 1 or 2 donor molecules, but several adducts show an unusual composition. Adducts containing 1,2 or 4 molecules of 1,4-dioxane as well as those with 1 or 3 molecules of 1,3-dioxane exhibit an unusually complex splitting of the copper signal in the epr spectrum which is believed to arise from magnetic dipole-dipole interactions of neighbouring copper ions. Stability constants of bis[1,1,1-trifluoro-4-phenylbuta-2,4-dionato]copper(II), of bis[1,1,1-trifluoro-4-(4′-fluorophenyl)-buta-2,4-dionato]copper(II) and of bis[1,1,1-trifluoro-4-(4′-methylphenyl)-buta-2,4-dionato]copper(II) with pyridine type bases have been determined spectrophotometrically. The obtained values indicate a considerable transmission of the electronic effects of the remote ring substituents to the copper ion and suggest coplanarity of the aromatic and the chelate rings in the adducts.

Keywords: Copper, dionates, adducts, esr spectra, stability constants.

INTRODUCTION

Our recent work on bis[1,1,1-trimethyl-4-phenylbuta-2,4-dionato]copper(II) and its derivatives[1] has focussed on the magnetic properties of their adducts. It has been shown that addition of 1,4-dioxane to one molecule of the copper compound results in a substantial degree of magnetic dilution between copper atoms in the pure solid so that unusual 9-line copper hyperfine splitting could be observed in the epr spectrum of powdered samples. Difficulties in growing crystals for single crystal epr and X-ray investigations, the relatively low stability of the 1,4-dioxane adducts and the question as to which molecular or structural factors are essential for the existence of the complex splitting in the epr spectrum of the adducts prompted us to extend our investigations to a variety of related systems. Adducts of bis[1,1,1-trifluoro-4-phenylbuta-2,4-dionato] copper(II) and its derivatives turned out to be promising for further studies since they are more thermodynamically stable and easier to obtain in a crystalline form than the corresponding bis[1,1,1-trimethyl-4-phenylbuta-2,4-dionato]copper(II) adducts. We report in this work the synthesis and properties of over 80 adducts of cyclic donors with bis[1,1,1-trifluoro-4-phenylbuta-2,4-dionato]copper(II) and its derivatives. Some of them show an unusually rich splitting in the epr spectrum in the crystalline state.

EXPERIMENTAL

The following abbreviations have been used throughout the paper: 1,1,1-Trifluoro-4-phenylbuta-2,4-dione, H(Hbta); 1,1,1-Trifluoro-4-(4′-methoxophenyl)-buta-2,4-dione, H(*p*-MeObta); 1,1,1-Trifluoro-4-(4′-methylphenyl)-buta-2,4-dione, H(*p*-Mebta);

1,1,1-Trifluoro-4-(4′-fluorophenyl)-buta-2,4-dione, H(p-Fbta); 1,1,1-Trifluoro-4-(4′-chlorophenyl)-buta-2,4-dione, H(p-Clbta); 1,1,1-Trifluoro-4-(4′-bromophenyl)-buta-2,4-dione, H(p-Brbta); 1,1,1-Trifluoro-4-(4′-nitrophenyl)-buta-2,4-dione, H[p-NO_2bta); 1, 1, 1-trifluoro-4-thienylbuta-2,4-dione, H(tta); 1,1,1-trifluoropenta-2,4-dione, H(tfa); 1,3-dioxane, 1,3-diox; 1,4-dioxane, 1,4-diox; tetrahydrofuran, THF; pyridine, py; pyrazine, pyr; methylpyridine, pic; dimethylpyridine, lut; morpholine, mor; 1,4-diazabicyclo-(2,2,2)-octane, ted.

Reagents

Reagent grade 1,4-dioxane, benzene, toluene, ethanol and methanol were purified by published methods.[2]

1,3-dioxane (Fluka AG) was dried over sodium wire and distilled, the fraction boiling at 101°C being collected. Tetrahydrofuran (POCH) was purified by refluxing with lithium aluminium hydride and distilled at 65–66°C. Morpholine (Loba Chemie), pyridine and its derivatives (Fluka AG) were dried over potassium hydroxide and distilled. The following fractions were collected: morpholine: 127–128°C; pyridine: 116–117°C; 2-methylpyridine: 129–130°C; 3-methylpyridine; 143°C; 4-methylpyridine: 144–145°C; 3,4-dimethylpyridine: 164–165°C; 3,5-dimethylpyridine 170°C. 1,4-diazabicyclo-(2,2,2)-octane (Koch-Light) and pyrazine (Loba Chemie) were recrystallized from benzene.

Preparation of β-diketones

1,1,1-Trifluoro-4-phenylbuta-2,4-dione and its derivatives were prepared by Claisen condensation of *para* substituted acetophenone with ethyl trifluoroacetate by the method previously described for the preparation of fluorinated β-diketones.[3]

Preparation of copper(II) β-diketonates

A filtered solution of copper(II) acetate monohydrate (0.025 mol) in hot water (100 cm^3) was added to the solution of the β-diketone (0.05 mol) in methanol (50 cm^3). The mixture was cooled and allowed to stand at 0°C for 2 hr. The resulting grey-green precipitate of the copper complex was filtered off, washed with a small quantity of ice-cold ethyl alcohol, recrystallized from ethyl alcohol then from chloroform and dried under vacuum over P_4O_{10} for 20 hrs.

Analytical and IR data, chromatograms, and melting points indicated that all the chelates were analytically pure.

Preparation of adducts

The 1,3-dioxane, 1,4-dioxane and THF adducts were prepared by recrystallization of the copper β-diketonates from these solvents. The separated solids were filtered off, washed with a small quantity of solvent and dried in air. Adducts obtained in this way contained not more than two molecules of solvent. Very slow evaporation of the solvent from Cu(p-MeObta)$_2$ solutions in 1,4-dioxane and Cu(p-NO_2bta)$_2$ solutions in 1,3-dioxane resulted in formation of adducts with 4 and 3 molecules of solvent, respectively.

To obtain a nitrogen base adduct, an excess of base dissolved in toluene was added slowly to a hot toluene solution of the copper β-diketonate. After cooling, grass-green crystals of the products separated out. They were filtered off, washed with a small quantity of toluene and dried over anhydrous magnesium sulphate.

The adduct Cu(p-NO$_2$bta)$_2$(mor)$_6$ was prepared as follows. 2.5 g (0.005 mol) of Cu(p-NO$_2$bta)$_2$ was dissolved in 45 cm^3 of freshly distilled morpholine. The solution, initially green, turned brown. After 24 hrs small crystals of a red-brown adduct separated. They were filtered off, washed with cold methanol and dried over anhydrous calcium chloride.

Preparation of 1,4-diazabicyclo-(2,2,2)-octane and pyrazine adducts was based on dissolving stoichiometric amounts of copper(II) ketoenolate and nitrogen base in hot benzene and subsequent cooling of the mixture. The separated crystals were filtered off, washed with benzene and dried over anhydrous magnesium sulphate.

Determination of nitrogen bases

In order to determine the content of a nitrogen base in an adduct, samples were dissolved in anhydrous acetic acid and titrated potentiometrically using 0.1 M H ClO$_4$ in anhydrous acetic acid using a glass/calomel electrode system. The aqueous solution of KCl in the calomel electrode was replaced by a LiCl solution in anhydrous acetic acid. For adducts of pyridine, methylpyridines, dimethylpyridines, morpholine and 1,4-diazabicyclo-(2,2,2)-octane the results were of high reproducibility. Six to eight titrations were made for each adduct.

Analytical data for all the adducts are listed in Tables I and II.

Apparatus and measurements

Elemental analysis data were obtained using a Carlo Erba MOD 1106 Elemental Analyser. Electronic spectra were recorded on Hitachi 356 M and on Cary 14

TABLE I
Analytical data for adducts of copper β-ketoenolates with oxygen donors and pyrazine

No	Compound	Found (Calcd), (%)						Decrease in weight at 160°C (%)	
		C		H		N			
1	Cu(Hbta)$_2$(1,4-diox)$_2$	50.2	(50.2)	4.22	(4.18)			25.6	(26.2)
2	Cu(p-Mebta)$_2$(1,4-diox)	51.3	(51.2)	3.87	(3.94)			14.7	(14.4)
3	Cu(p-MeObta)$_2$(1,4-diox)	48.4	(48.6)	3.77	(3.74)			13.7	(13.7)
4	Cu(p-MeObta)$_2$(1,4-diox)$_2$							24.0	(24.1)
5	Cu(p-MeObta)$_2$(1,4-diox)$_4$							36.1	(38.6)
6	Cu(p-Fbta)$_2$(1,4-diox)$_2$	47.3	(47.6)	3.66	(3.68)			23.9	(24.9)
7	Cu(p-Clbta)$_2$(1,4-diox)	44.3	(44.3)	2.80	(2.77)			13.9	(13.8)
8	Cu(p-Brbta)$_2$(1,4-diox)	39.0	(39.0)	2.41	(2.43)			12.0	(12.0)
9	Cu(p-NO$_2$bta)$_2$(1,4-diox)$_2$	44.2	(44.3)	3.44	(3.42)	3.66	(3.68)	23.1	(23.1)
10	Cu(p-NO$_2$bta)$_2$(1,3-diox)	42.9	(42.7)	2.76	(2.67)	4.30	(4.15)	13.6	(13.7)
11	Cu(p-NO$_2$bta)$_2$(1,3-diox)$_3$							31.8	(31.2)
12	Cu(p-NO$_2$bta)$_2$(THF)	43.9	(43.9)	2.78	(2.75)	4.54	(4.27)	11.0	(11.0)
13	Cu(Hbta)$_2$(pyr)							14.1	(14.0)
14	Cu(p-Mebta)$_2$(pyr)							13.4	(13.3)
15	Cu(p-MeObta)$_2$(pyr)							12.7	(12.6)
16	Cu(p-Fbta)$_2$(pyr)							13.1	(13.1)
17	Cu(p-Clbta)$_2$(pyr)							12.5	(12.5)
18	Cu(p-Brbta)$_2$(pyr)							11.0	(10.9)
19	Cu(p-NO$_2$bta)$_2$(pyr)							12.1	(12.1)

TABLE II
Analytical data for adducts of copper(II) benzoyltrifluoroacetonate and its derivatives with nitrogen bases.

No	Compound	% base		No	Compound	% base	
		Found	Calcd			Found	Calcd
1	Cu(Hbta)$_2$(py)$_2$	24.5 ± 0.2	24.3	33	Cu(*p*-Brbta)$_2$(3.4-lut)$_2$	24.9 ± 0.1	24.8
2	Cu(*p*-Mebta)$_2$(py)	13.1 ± 0.1	13.2	34	Cu(*p*-NO$_2$bta)$_2$(3.4-lut)$_2$	26.9 ± 0.2	26.8
3	Cu(*p*-MeObta)$_2$(py)	12.4 ± 0.1	12.5	35	Cu(Hbta)$_2$(3.5-lut)$_2$	30.6 ± 0.2	30.3
4	Cu(*p*-Fbta)$_2$(py)	13.3 ± 0.2	13.0	36	Cu(*p*-Mebta)$_2$(3.5-lut)$_2$	28.9 ± 0.1	29.1
5	Cu(*p*-Clbta)$_2$(py)$_2$	22.2 ± 0.1	21.9	37	Cu(*p*-MeObta)$_2$(3.5-lut)$_2$	28.1 ± 0.1	27.9
6	Cu(*p*-Brbta)$_2$(py)$_2$	19.4 ± 0.2	19.5	38	Cu(*p*-Fbta)$_2$(3.5-lut)$_2$	29.1 ± 0.2	28.8
7	Cu(*p*-NO$_2$bta)$_2$(py)$_2$	21.5 ± 0.1	21.3	39	Cu(*p*-Clbta)$_2$(3.5-lut)$_2$	27.9 ± 0.2	27.6
8	Cu(Hbta)$_2$(2-pic)	15.9 ± 0.1	15.9	40	Cu(*p*-Brbta)$_2$(3.5-lut)$_2$	24.9 ± 0.1	24.8
9	Cu(*p*-Mebta)$_2$(2-pic)	15.3 ± 0.1	15.1	41	Cu(*p*-NO$_2$bta)$_2$(3.5-lut)$_2$	27.0 ± 0.2	26.8
10	Cu(*p*-Fbta)$_2$(2-pic)	15.2 ± 0.1	15.0	42	[Cu(Hbta)$_2$]$_2$(ted)	9.8 ± 0.1	10.2
11	Cu(*p*-Clbta)$_2$(2-pic)	14.4 ± 0.1	14.2	43	[Cu(*p*-Mebta)$_2$]$_2$(ted)	9.5 ± 0.1	9.7
12	Cu(*p*-Brbta)$_2$(2-pic)	12.5 ± 0.1	12.5	44	[Cu(*p*-MeObta)$_2$]$_2$(ted)	8.9 ± 0.1	9.2
13	Cu(*p*-NO$_2$bta)$_2$(2-pic)	13.6 ± 0.1	13.8	45	[Cu(*p*-Fbta)$_2$]$_2$(ted)	9.5 ± 0.1	9.6
14	Cu(Hbta)$_2$(3-pic)$_2$	27.4 ± 0.1	27.4	46	[Cu(*p*-Clbta)$_2$]$_2$(ted)	8.9 ± 0.1	9.1
15	Cu(*p*-Mebta)$_2$(3-pic)	15.1 ± 0.1	15.1	47	[Cu(*p*-Brbta)$_2$]$_2$(ted)	7.6 ± 0.1	7.9
16	Cu(*p*-MeObta)$_2$(3-pic)	14.5 ± 0.1	14.4	48	[Cu(*p*-NO$_2$bta)$_2$]$_2$(ted)	8.6 ± 0.1	8.8
17	Cu(*p*-Fbta)$_2$(3-pic)	15.2 ± 0.1	14.9	49	Cu(Hbta)$_2$(ted)	18.0 ± 0.1	18.5
18	Cu(*p*-Clbta)$_2$(3-pic)$_2$	25.0 ± 0.2	24.9	50	Cu(*p*-Mebta)$_2$(ted)	17.0 ± 0.2	17.7
19	Cu(*p*-Brbta)$_2$(3-pic)$_2$	22.3 ± 0.1	22.2	51	Cu(*p*-MeObta)$_2$(ted)	16.0 ± 0.1	16.8
20	Cu(*p*-NO$_2$bta)$_2$(3-pic)$_2$	24.2 ± 0.1	24.2	52	Cu(*p*-Fbta)$_2$(ted)	17.1 ± 0.2	17.5
21	Cu(Hbta)$_2$(4-pic)$_2$	27.5 ± 0.1	27.4	53	Cu(*p*-Clbta)$_2$(ted)	16.0 ± 0.1	16.6
22	Cu(*p*-Mebta)$_2$(4-pic)	15.3 ± 0.1	15.1	54	Cu(*p*-Brbta)$_2$(ted)	14.2 ± 0.1	14.7
23	Cu(*p*-MeObta)$_2$(4-pic)	14.6 ± 0.1	14.4	55	Cu(*p*-NO$_2$bta)$_2$(ted)	16.2 ± 0.1	16.1
24	Cu(*p*-Fbta)$_2$(4-pic)	14.9 ± 0.1	15.0	56	Cu(Hbta)$_2$(mor)$_2$	26.3 ± 0.2	27.0
25	Cu(*p*-Clbta)$_2$(4-pic)$_2$	24.6 ± 0.2	24.9	57	Cu(*p*-Mebta)$_2$(mor)	13.8 ± 0.1	14.3
26	Cu(*p*-Brbta)$_2$(4-pic)$_2$	22.1 ± 0.1	22.2	58	Cu(*p*-MeObta)$_2$(mor)	13.1 ± 0.1	13.6
27	Cu(*p*-NO$_2$bta)$_2$(4-pic)$_2$	24.3 ± 0.1	24.2	59	Cu(*p*-Fbta)$_2$(mor)	13.7 ± 0.1	14.1
28	Cu(Hbta)$_2$(3.4-lut)$_2$	30.3 ± 0.2	30.3	60	Cu(*p*-Clbta)$_2$(mor)	13.1 ± 0.1	13.4
29	Cu(*p*-Mebta)$_2$(3.4-lut)$_2$	29.0 ± 0.1	29.1	61	Cu(*p*-Brbta)$_2$(mor)	12.0 ± 0.1	11.8
30	Cu(*p*-MeObta)$_2$(3.4-lut)$_2$	28.0 ± 0.1	27.9	62	Cu(*p*-NO$_2$bta)$_2$(mor)	13.4 ± 0.1	13.0
31	Cu(*p*-Fbta)$_2$(3.4-lut)$_2$	28.7 ± 0.1	28.8	63	Cu(*p*-NO$_2$bta)$_2$(mor)$_6$	47.1 ± 0.2	47.2
32	Cu(*p*-Clbta)$_2$(3.4-lut)$_2$	27.6 ± 0.1	27.6				

instruments. IR spectra were obtained using a Perkin Elmer Model 621 instrument. Spectra of solid samples were recorded as nujol or hexachlorobutadiene mulls. Magnetic susceptibilities were determined in the 4–300 K range using a Cahn magnetic balance. Diamagnetic corrections were made by employing Pascal's constants. Potentiometric titrations were performed using a Radelkis Model OP-205 precision pH meter. Thermogravimetric curves were obtained on a Paulik-Paulik type OD 103 Derivatograph using aluminium oxide as the reference. Epr spectra were obtained using a JES-ME-3X spectrometer working at 9 and 25 GHz (K-band). Molecular weights were determined in a vapour pressure osmometer (Model 201 A). The absorption spectra of solutions were measured in 1 cm vapour proof cells placed in a constant temperature cell housing.

RESULTS AND DISCUSSION

The copper chelates Cu(*p*-MeObta)$_2$, Cu(Hbta)$_2$, Cu(*p*-Mebta)$_2$, Cu(*p*-Fbta)$_2$, Cu(*p*-Clbta)$_2$, Cu(*p*-Brbta)$_2$ and Cu(*p*-NO$_2$bta)$_2$ easily form adducts with almost all the donors investigated in this work. The number of donor molecules which remained after

TABLE III

Number of donor molecules per copper atom in adducts of copper(II) with *p*-substituted-benzoyltrifluoroacetonates and oxygen or nitrogen donors.

Donor	1,4-diox	1,3-diox	THF	pyr	py	3-pic	2-pic	4-pic	3,4-lut	3,5-lut	mor	ted
$pK_a^{\dagger}$ *p*-substituent	−3.22	−2.08	0.6	5.24	5.76	5.95	6.04	6.65	6.24	8.55		
MeO	1 2 4			1	1	1		1	2	2	1	0.5 1
Me	1			1	1	1	1	1	2	2	1	0.5 1
H	2			1	2	2	1	2	2	2	2	0.5 1
F	2			1	2	2	1	2	2	2	1	0.5 1
Cl	1			1	2	2	1	2	2	2	1	0.5 1
Br	1			1	2	1	2	2	2	2	1	0.5 1
NO_2	1 2	1 3	1	1	2	1	2	2	2	2	1	0.5 6

[†] Refs. 12–14

washing the solid with solvent and drying at 25°C is given in Table III. Adducts containing 1,3-dioxane and tetrahydrofuran decomposed at 25°C to give unsolvated products except with the Cu(p-NO_2bta)$_2$ adducts which retained one molecule of tetrahydrofuran or one to three molecules of 1,3-dioxane. The enhanced acceptor properties of Cu(p-NO_2bta)$_2$ seem to be due to the electron withdrawing effect of the remote nitro group. Tetrahydrofuran is a stronger base than 1,4-dioxane as may be inferred from donicities (THF = 20 1,4-dioxane=14.8)[4] or pK_a values.[14] Nevertheless, 1,4-dioxane adducts are more stable than those of tetrahydrofuran or 1,3-dioxane. The 1:1 1,4-dioxane adducts are a little more thermally stable than the 1:2 adducts (Figure 1).

The 1:2 1,4-dioxane adducts lose the coordinated dioxane molecules gradually when heated, except with Cu(Hbta)$_2$(1,4-diox)$_2$ which forms a 1:1 adduct as an intermediate. Somewhat higher thermal stability of the 1:1 1,4-dioxane adducts suggests coordination of 1,4-dioxane molecule through both oxygen atoms. Very recently we have shown[5] that in the 1:1 adduct of Cu(p-NO_2bta)$_2$ with 1,4-dioxane, the 1,4-dioxane molecules are bridging ligands which link two copper ions to form an infinite one dimensional polymer. Similar coordination seems to occur in other 1:1 adducts of 1,4-dioxane. In 1:2 adducts, however, the 1,4-dioxane molecule sems to act as a monodentate ligand. The 1,4-dioxane molecules coordinated through one oxygen atom have been found recently[5] in [Cu(p-MeObta)$_2$(1,4-diox)$_2$] (1,4-diox)$_2$. All the pyrazine adducts decompose above 130°C losing the coordinated base. Morpholine forms green 1:1 adducts and one red adduct of composition Cu(p-NO_2bta)$_2$(mor)$_6$.

Maxima of the long wavelength bands in the electronic spectrum of the 1:1 adducts containing 2-methylpyridine, pyrazine and of the 1:0.5 adduct of 1,4-diazabicyclo-(2,2,2)-octane occur in the range 630–680 nm. Positions of the bands and their shapes resemble that of the 1:1 quinoline adduct of copper(II) acetylacetonate with a maximum at $\lambda = 650$ nm. The structural X-ray analysis of the adduct showed square

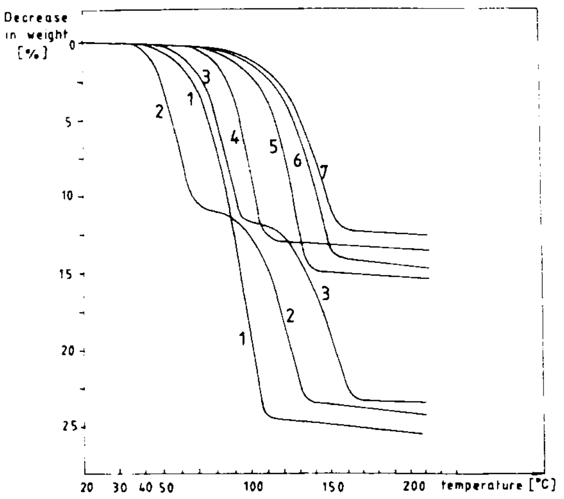

FIGURE 1 Thermogravimetric curves for adducts of copper complexes with 1,4-dioxane: (1)=$Cu(Hbta)_2(1,4\text{-}diox)_2$, (2) = $Cu(p\text{-}Fbta)_2(1,4\text{-}diox)_2$, (3) = $Cu(p\text{-}NO_2bta)_2(1,4\text{-}diox)_2$, (4) = $Cu(p\text{-}MeObta)_2$ (1,4-diox),(5) = Cu(p-Mebta)(1,4-diox), (6) = $Cu(p\text{-}Clbta)_2(1,5\text{-}diox)$, (7) = $Cu(p\text{-}Brbta)_2(1,4\text{-}diox)$.

pyramidal arrangements of coordinating atoms around the copper ion.[6] Preliminary results of an X-ray investigation of $[Cu(Hbta)_2]_2(ted)$ showed that it is a binuclear compound in which both copper ions are five-coordinated and link both nitrogen atoms of 1,4-diazabicyclo-(2,2,2)-octane.[7] For the 1:2 adducts of pyridine type bases and for the 1:1 ted adducts the long wavelength band occurs at longer wavelengths λ_{max} = 700–740 nm and resembles bands of the six-coordinated copper β-diketonate adducts $Cu(tta)_2(4\text{-}pic)_2$ with λ_{max} = 740 nm and $Cu(tfa)_2(4\text{-}pic)_2$ with λ_{max} = 730 nm.[8] Six coordination of copper in the 1:1 adducts of 1,4-diazabicyclo-(2,2,2)-octane may be achieved if each copper atom coordinates two ted molecules and each ted molecule links two copper atoms to form an infinite polymer. The long wavelength band in $Cu(p\text{-}NO_2bta)_2(mor)_6$ is shifted in a direction opposite to that expected for copper

TABLE IV
Position of the long wavelength band in the reflectance spectrum of adducts of copper p-nitrobenzoyltrifluoroacetonate with various donors

No	Compound	λ_{max} (nm)
1	$Cu(p\text{-}NO_2bta)_2(1,4\text{-}diox)_2$	630
2	$Cu(p\text{-}NO_2bta)_2(2\text{-}pic)$	630
3	$Cu(p\text{-}No_2bta)_2(pyr)$	650
4	$Cu(p\text{-}NO_2bta)_2(3\text{-}pic)_2$	700
5	$Cu(p\text{-}NO_2bta)_2(4\text{-}pic)_2$	700
6	$Cu(p\text{-}NO_2bta)_2(3,4\text{-}lut)_2$	725
7	$Cu(p\text{-}NO_2bta)_2(3,5\text{-}lut)_2$	700
8	$Cu(p\text{-}NO_2bta)_2(mor)_6$	530
9	$[Cu(p\text{-}NO_2bta)_2]_2(ted)$	680
10	$Cu(p\text{-}NO_2bta)_2(ted)$	735

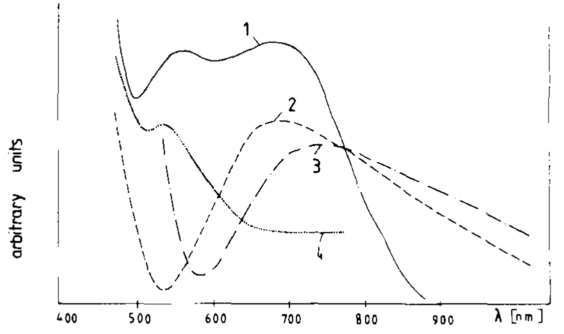

FIGURE 2 Reflectance spectra of: (1) = Cu(p-NO_2bta)$_2$, (2) = [Cu(p-NO_2bta)$_2$]$_2$(ted), (3) = Cu(p-NO_2bta)$_2$(ted), (4) = Cu(p-NO_2bta)$_2$(mor)$_6$.

β-diketonate adducts with nitrogen bases.[9] The position of maximum absorption at λ = 530 nm suggests a stronger ligand field than in other adducts and is probably due to coordination of the copper ion to nitrogen atoms of morpholine molecules. Many years ago Bush *et al.*,[10] determined the structure of the adduct of copper(II) hexafluoroacetylacetonate with 2 molecules of *N*, *N*-dimethyl-1,2-diaminoethane and found that the copper ion is coordinated by four nitrogen atoms and that the maximum of absorption in the visible spectrum is at 536 nm. Coordination of nitrogen in Cu(p-NO_2bta)$_2$(mor)$_6$ might result in a partial or total replacement of β-diketonato anions by morpholine in the inner coordination sphere. Consistent with this suggestion seems to be a relative higher carbonyl stretching frequency (1640 cm^{-1}) in the adduct as compared to free Cu(p-NO_2bta)$_2$ (1612 cm^{-1}). Formation of the 1:1 adducts with morpholine results in a shift of the N-H stretching frequencies of the base to lower values. This low-frequency shift is consistent with *N*-coordination. Magnetic moments for the adducts are in the range expected for copper(II) with $S = 1/2$. Selected examples are given in Table VI.

Magnetic susceptibilities of Cu(Hbta)$_2$ and its derivative adducts with various donors have been studied in the 4–300 K temperature range. Almost all the adducts obeyed the Curie-Weiss law. A small deviation of linearity was observed for the 1:0.5 1,4-diazabicyclo-(2,2,2)-octane adducts [Cu(Hbta)$_2$]$_2$(ted), [Cu(p-Fbta)$_2$]$_2$(ted) and [Cu(p-Brbta)$_2$]$_2$(ted).

Using the Bleaney-Bowers equation for these adducts[11] we obtain similar values of the exchange integral, $J = -3 \pm 1$ cm^{-1}. The small negative value indicates a weak

TABLE V
N-H stretching vibrations in neat morpholine and its adducts.

No	Compound	N-H (cm^{-1})
1	Morpholine	3330
2	Cu(p-MeObta)$_2$(mor)	3260
3	Cu(p-Mebta)$_2$(mor)	3220
4	Cu(Hbta)$_2$(mor)$_2$	3270
5	Cu(p-Fbta)$_2$(mor)	3260
6	Cu(p-Clbta)$_2$(mor)	3260
7	Cu(p-NO_2bta)$_2$(mor)	3260

TABLE VI
Room temperature magnetic moments of adducts of copper(II) with *p*-substituted-benzoyltrifluoroacetonates and various donors.

No	Compound	Magnetic moment (B.M.)
1	$Cu(Hbta)_2(1,4\text{-}diox)_2$	1.84
2	$Cu(p\text{-}Fbta)_2(1,4\text{-}diox)_2$	1.86
3	$Cu(p\text{-}Brbta)_2(1,4\text{-}diox)$	1.83
4	$Cu(p\text{-}NO_2bta)_2(THF)$	1.81
5	$Cu(p\text{-}NO_2bta)_2(1,3\text{-}diox)$	1.76
6	$Cu(p\text{-}NO_2bta)_2(py)$	1.98
7	$Cu(p\text{-}NO_2bta)_2(pyr)$	1.98
8	$[Cu(p\text{-}NO_2bta)_2]_2(ted)$	1.98
9	$Cu(p\text{-}NO_2bta)_2(ted)$	1.99

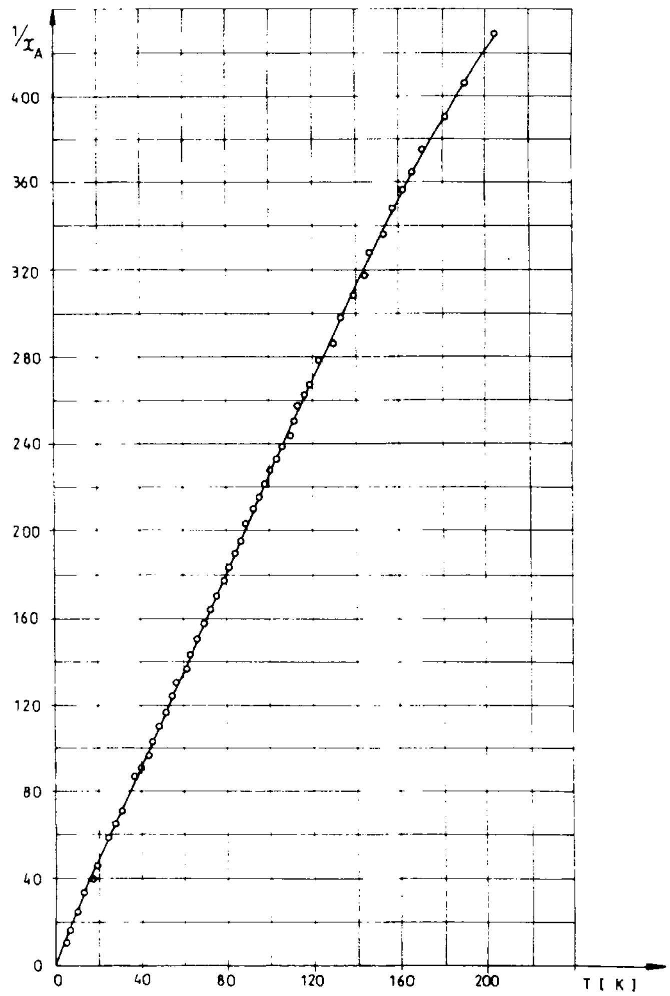

FIGURE 3 Plot of the inverse of magnetic susceptibility *versus* temperature for $[Cu(Hbta)_2]_2(ted)$.

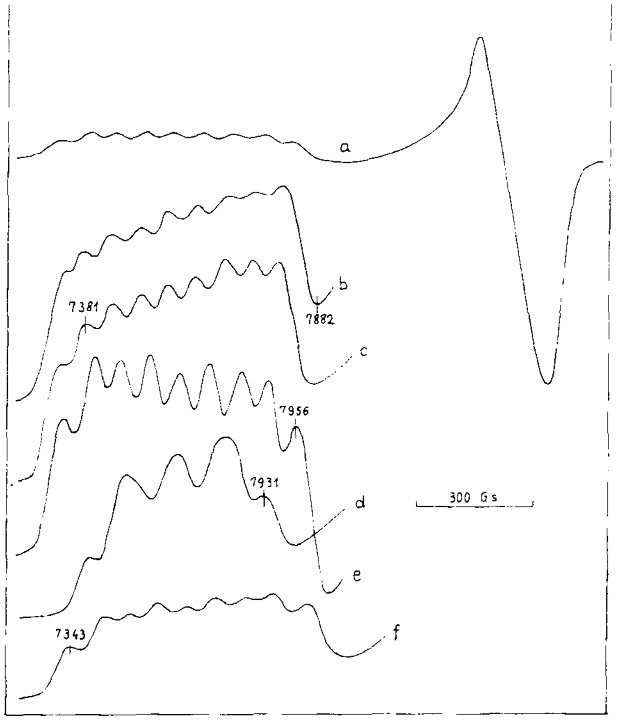

FIGURE 4 K-band e.p.r. spectra of powdered samples of: (a) = Cu(p-MeObta)$_2$(1,4-diox); parts of K-band e.p.r. spectra after expansion of powdered: (b) = Cu(p-Clbta)$_2$(1,4-diox), (c) = Cu(p-NO$_2$bta)$_2$(1,4-diox)$_2$, (d) = Cu(p-NO$_2$bta)$_2$(1,3-diox), (e) = Cu(p-MeObta)$_2$(1,4-diox)$_2$, (f) = Cu(Hbta)$_2$(1,4-diox)$_2$.

antiferromagnetic coupling.

E.p.r. spectra of all the polycrystalline adducts have been recorded. In spite of the large number of adducts investigated by this technique, only in a few cases was an unusually rich splitting of the e.p.r. signal observed. It occurred in adducts containing coordinated 1,4-dioxane or 1,3-dioxane irrespective on the number of solvent molecules in the adduct. Removal of coordinated 1,4-dioxane or 1,3-dioxane resulted in a total disappearance of the splitting. A seven line pattern was observed in the spectra of [Cu(Hbta)$_2$]$_2$(ted), [Cu(p-Fbta)$_2$]$_2$(ted) and [Cu(p-Brbta)$_2$]$_2$(ted).

To elucidate the origin of the e.p.r. signals in the magnetically undiluted 1,4-dioxane adducts, single crystal X-ray and single crystal e.p.r. studies have been recently carried out.[5] It has been shown that in [Cu(p-MeObta)$_2$(1,4-diox)$_2$](1,4-diox)$_2$ and in Cu(p-NO$_2$bta)$_2$(1,4-diox) the splitting of the e.p.r. signals is due to magnetic dipole-dipole interactions. Exchange is found to be slow and largely reduced due to large copper-copper separations.

Results of the preset work indicate that 1,4-dioxane, 1,3-dioxane and 1,4-diazabicyclo-(2,2,2)-octane occupy a particular position among the donors studied. Rich patterns in the e.p.r. spectra of their adducts suggests that addition of these donors to copper β-diketonates results in formation of moderately magnetically dilute systems in which the individual paramagnetic ions are at a favourable separation so that weak dipole-dipole or exchange interactions are not obscured in the spectrum by line broadening effects. Recent crystallographic studies show that the shortest copper-

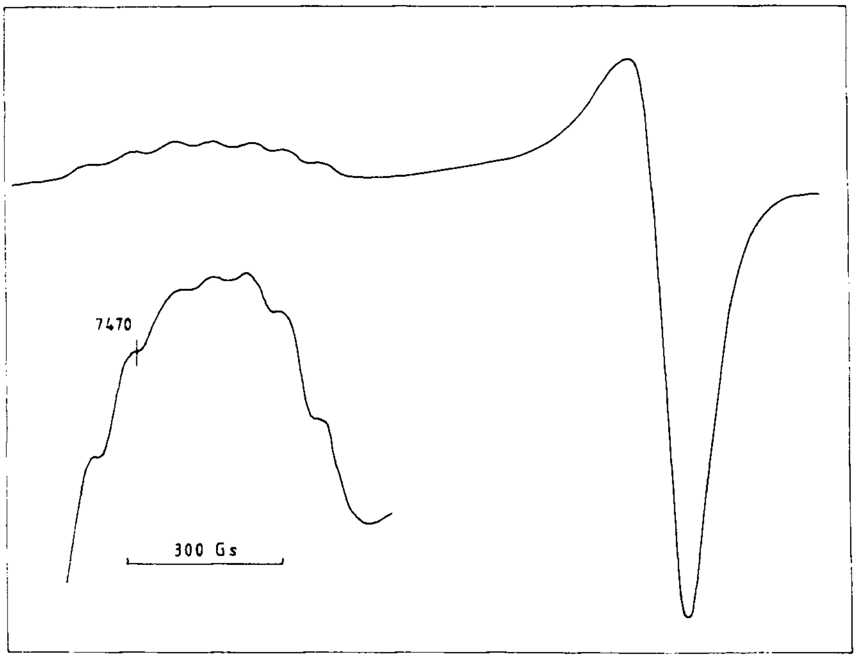

FIGURE 5 K-band e.p.r. spectrum of a powdered sample of $[Cu(Hbta)_2]_2(ted)$.

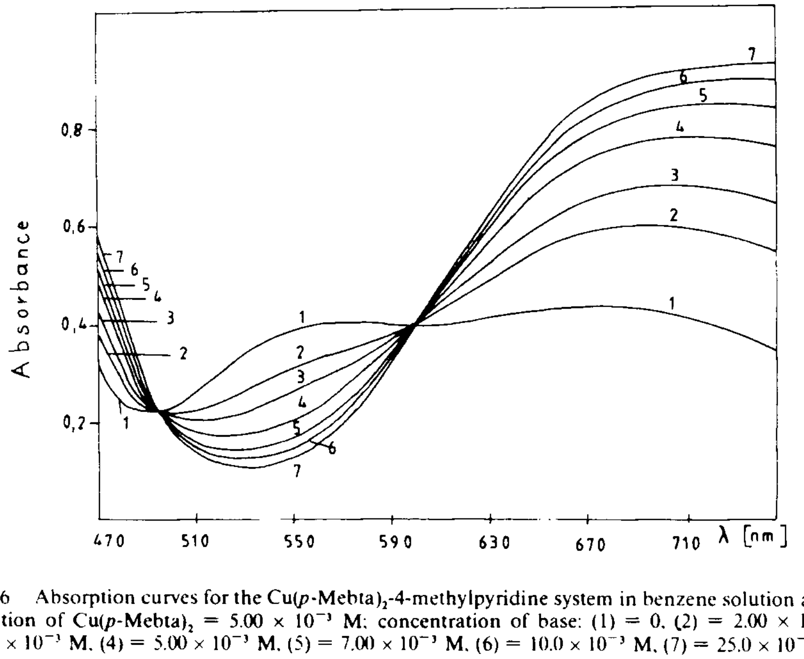

FIGURE 6 Absorption curves for the Cu(*p*-Mebta)$_2$-4-methylpyridine system in benzene solution at 25°C: concentration of Cu(*p*-Mebta)$_2$ = 5.00×10^{-3} M; concentration of base: (1) = 0, (2) = 2.00×10^{-3} M, (3) = 3.00×10^{-3} M, (4) = 5.00×10^{-3} M, (5) = 7.00×10^{-3} M, (6) = 10.0×10^{-3} M, (7) = 25.0×10^{-3} M.

copper separations in adducts which display the unusually rich pattern are 8.09Å in $[Cu(p\text{-}MeObta)_2(1,4\text{-}diox)_2](1,4\text{-}diox)_2$,[5] 7.6 Å in $Cu(p\text{-}NO_2bta)_2(1,4\text{-}diox)$,[5] and 6.5Å in $[Cu(Hbta)_2]_2(ted)$.[7]

Data in Table III show that mixtures of copper complexes and pyridine type bases in inert solvents give either 1:1 or 1:2 adducts. Higher tendency to form 1:2 adducts was shown generally in copper complexes containing electron withdrawing substituents. The higher acceptor properties of these complexes suggested a transmission of electronic effects of the remote *para* substituents to the copper ion thus increasing its acceptor properties. In order to assess the extent of this transmission and to obtain information on the thermodynamic stability of the adducts, we determined stability constants for the 1: adducts of bis[1,1,1-trifluoro-4(4′-methylphenly)-buta-2,4-dionato] copper(II), bis[1,1,1-trifluoro-4-phenylbuta-2,4-dionato]copper(II) and bis[1,1,1-trifluoro-4(4′-fluorophenyl)-buta-2,4-dionato]copper(II) with pyridine, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 3,4-dimethylpyridine, 3,5-dimethylpyridine, pyridine-*N*-oxide and 4-methylpyridine-*N*-oxide.

The reasons for choice of the above donors and complexes was the relatively good solubility of substrates and products in benzene.

Molecular weight determinations show that $Cu(p\text{-}Mebta)_2$, $Cu(Hbta)_2$ and $Cu(p\text{-}Fbta)_2$ are monomeric in benzene solution. They react with pyridine, pyridine-*N*-oxide and their derivatives to give adducts in dilute solution when appropriate ratios of donor to acceptor are preserved. This is shown by well defined isosbestic points and the constancy of the equilibrium constant calculated under the assumption that only one complex (1:1) is formed. A set of absorption curves for one system is given in Figure 6. The adduct formation constants, K_{add}, have been determined numerically[15] from the absorption data obtained at 740 nm. The calculated values of K_{add} and the pK_a values of the bases are listed in Table VII. This data shows that donor properties of bases *versus* copper chelates increase in the order 2-methylpyridine < pyridine-*N*-oxide <4-methylpyridine-*N*-oxide < pyridine < 3-methylpyridine < 4-methylpyridine < 3,5-dimethylpyridine < 3,4-dimethylpyridine. A plot of the logarithm of the adduct formation constant for pyridine and its methyl derivatives shows that where steric hindrance to adduct formation is an unimportant factor the log K_{add} values vary linearly with the pK_a values of bases. Least-squares treatment of the data listed in Table VII for adducts of pyridine, 3-methylpyridine, 4-methylpyridine, 3,5-dimethylpyridine and 3,4-dimentylpyridine lead to the following relations

$$\log K_{add} = 0.08 + 0.51\ pK_a\ (r{=}0.98) \text{ for } Cu(p\text{-}Mebta)_2 \text{ adducts,}$$

$$\log K_{add} = 0.24 + 0.52\ pK_a\ (r{=}0.95) \text{ for } Cu(Hbta)_2 \text{ adducts, and}$$

$$\log K_{add} = 0.31 + 0.51\ pK_a\ (r{=}0.99) \text{ for } Cu(p\text{-}Fbta)_2 \text{ adducts,}$$

where r is the linear correlation factor.

An inspection of Table VII data indicates that in spite of small differences in substituent constants for *para* substituents ($\sigma_{CH_3} = -0.17$, $\sigma_F = +0.06$[16]) there is a marked increase in stability constant on going from $Cu(p\text{-}Mebta)_2$ to $Cu(p\text{-}Fbta)_2$ adducts. The difference between the first right-hand side terms of the first and the third equations corresponds roughly to the difference in sigma values of substituents. These observations suggest a high transmission of electronic effects of ring substituents *via* the aromatic and chelate rings to the copper atom thus influencing its acceptor properties. High transmission indicates that both the aromatic and the chelate rings are coplanar and conjugated in solution.

Adduct formation constants of *N*-oxides are *ca* 80 times higher than the values calculated from the above equations on the basis of pK_a values. An increase in K_{add} on

TABLE VII

Adduct formation constants, K_{add}, in benzene at 25°C.

No	Base	pK_a	Adducts of Cu(p-Mebta)$_2$		Cu(Hbta)$_2$		Cu(p-Fbta)$_2$	
			10^{-2} K_{add}	$\Delta\varepsilon^{f}$	10^{-2} K_{add}	$\Delta\varepsilon^{f}$	10^{-2} K_{add}	$\Delta\varepsilon^{f}$
1	Pyridine	5.31^{a}	5.89 ± 0.15	53.9 ± 0.4^{c}	8.13^{g}		9.33 ± 0.3	49.2 ± 0.2^{c}
2	2-Methylpyridine	6.03^{a}	3.48 ± 0.02	53.2 ± 1.1^{c}	2.69^{g}		2.88 ± 0.2	53.7 ± 0.3^{c}
3	3-Methylpyridine	5.76^{a}	10.0 ± 0.06	58.4 ± 0.6^{c}	14.8^{g}		15.8 ± 0.3	61.4 ± 0.1^{c}
4	4-Methylpyridine	6.12^{a}	14.4 ± 0.9	59.7 ± 0.8^{d}	30.2^{g}		25.7 ± 0.6	63.8 ± 0.2^{d}
5	3,4-Dimethylpyridine	6.81^{a}	24.0 ± 1.9	65.6 ± 0.4^{d}	35.5 ± 0.4	45.7 ± 0.4^{d}	38.0 ± 1.0	64.5 ± 0.3^{d}
6	3,5-Dimethylpyridine	6.23^{a}	18.6 ± 0.4	64.0 ± 0.4^{d}	21.9 ± 0.3	41.8 ± 0.6^{d}	26.9 ± 0.4	63.8 ± 0.3^{d}
7	Pyridine-*N*-oxide	0.60^{b}	2.04 ± 0.08	26.6 ± 0.6^{e}	2.88 ± 0.11	25.8 ± 0.6^{e}	3.47 ± 0.1	28.7 ± 0.5^{e}
8	4-Methylpyridine-*N*-oxide	1.09^{b}	3.09 ± 0.08	34.0 ± 0.6^{e}	4.79 ± 0.36	33.8 ± 0.8^{e}	5.37 ± 0.2	34.7 ± 0.5^{e}

[a] Reference 16; [b] reference 17; [c] 720 nm; [d] 740 nm; [e] 700 nm; [f] $\Delta\varepsilon$ is the difference between the absorption coefficients of the Cu(p-Xbta)$_2$ – base adduct and of free Cu(p-Xbta)$_2$; [g] reference 18.

going from the pyridine-*N*-oxide adducts to the 4-methylpyridine-*N*-oxide adducts indicates that the dominant role in coordination involves ligand-to-metal donation. Back donation of electrons from the filled metal d orbitals to the π^* antibonding orbitals of the N-O bond in the ligand seems to be of less importance.

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