Coordination Compounds of Benzotriazole and Related Ligands

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The coordination chemistry of benzotriazole towards several transition metal compounds has been studied. Unpon reaction of neutral benzotriazole (BTAH) with metal compounds under varying conditions, both neutral (BTAH) ligands and anionic, deprotonated ligands (BTA⁻) may be coordinated to the metal.

The compounds have the general formula M-(BTAH)ₙXₘ, with M = Cu, Zn, Cd, Hg, Pd, Ti, Sn, n = 1, 2, 3, 4, X = Cl, Br and m = 2 or 4. Similar compounds of formula Cu(ligand)ₙX₂ (X = Cl, Br; n = 1, 2) with 5-nitrobenzotriazole and N-methylbenzotriazole, were obtained. Compounds with anionic BTA have the formulae: Cu(BTA)Cl, Cu(BTA)₁.₅-(BF₄)₀.₅, Cu(BTA)₂, Hg(BTA)₂, Cu(phen)₂(BTA)₂, Hg(BTA)(CH₃), Si(BTA)(CH₃)₃, Mn(BTA)(CO)₅. In addition some mixed compounds were isolated, i.e. Cu₂(BTA)₂(BTAH)(NO₃)₂, Cu₂(BTA)(BTAH)(SO₄) and Ni(BTAH)(BTA)(BF₄).

Structures of the compounds have been proposed based on infrared and far-infrared spectroscopy, ligand field and UV spectroscopy, EPR spectroscopy, conductivity data and NMR spectroscopy.

The most common mode of bonding for neutral, monodentate benzotriazole to metal ions seems to involve N(3) in BTAH (this is named N(1) in BTA). In the case of bidentate binding, it is not clear whether N(1)–N(2) or N(1)–N(3) bidentate bridging occurs. Spectral measurements are unable to distinguish between these modes. Tridentate binding of salt-like structures seems likely for Cu(BTA)₂ and Hg(BTA)₂, and might be present in a few other compounds such as Cu(BTA)Cl. Due to the insoluble nature of most of the compounds, polymeric structures using BTA and BTAH as bridging ligands seem to occur most frequently. Such structures are discussed in relation to the corrosion-inhibiting properties of benzotriazole.

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Introduction

Benzotriazole, *1* (BTAH; the conjugate base is represented by BTA, see Fig. 1) is a technologically important corrosion inhibitor for copper, copper alloys and a few other metals [1–5]. By treating copper surfaces with benzotriazole (from aqueous solution, using BTAH-impregnated wrapping paper, or from the vapour) the ligand is strongly absorbed and produces a surface film which acts as a barrier to cathodic reactions [1–7]. At low pH values, *i.e.* below pH = 2, the inhibitor action decreases. The nature of the surface layer and its thickness have been the subject of several investigations [2–4, 8, 9]. Both Cu(I)–BTA and Cu(II)–BTA compounds have been considered to be present in the surface layers [9–11]. In the earlier literature, some impure Cu(I)–BTA and Cu(II)–BTA compounds were described, as well as some containing Ni(II), Co(II) and Pd(II) [12–14]. More recently, some Mn(II) compounds [15] and a group of compounds having the formula Pd(BTAH)₂X₂ were described [16]. The crystal structure of two trimeric species M₃(BTA)₆(allyl amine)₆(Ph₃PO)₂ (M = Co, Ni) showed the presence of BTA⁻ ligands coordinated in a bridging manner via N(1) and N(2), [17]. Bridging via N(1) and N(3) was recently observed in a Cu(II) dimer by Hendriks [18]. Tridentate bridging coordination using N(1), N(2) and N(3) has recently been established in the mixed-valence cluster compounds Cu₅(BTA)₆-(RNC)₄ [19]. Such a cluster has been proposed for Cu₅(BTA)₆(acac)₄ by Marshall [20].

We have reported monodentate N(1) coordination in Ir(CO)(PPh₃)₂(BTA), [21], as well as tridentate

Fig. 1. Structures of two tautomers of benzotriazole (BTAH), *1*. The deprotonated species is abbreviated as BTA.

bridging coordination for Tl(BTA) [22]. [CuCl-(BTAH)]$_4$ was described recently in a study on its luminescence [23]. Very recently, after completion of our experiments, Søtofte and Nielsen [24–26] have reported X-ray crystal structures of [CuCl$_2$-(BTAH)$_2$]$_2$·H$_2$O, ZnCl$_2$(BTAH)$_2$, Zn$_2$(BTA)$_4$ and Ni$_3$(BTA)$_6$(NH$_3$)$_6$·2(CH$_3$)$_2$CO·2H$_2$O. Thus the possibility of coordination of benzotriazolate through all three nitrogens, as well as the possibility of coordination by neutral BTAH, has been demonstrated by X-ray diffraction. The sheer multiplicity of non-mutually exclusive bonding modes for BTAH and BTA makes precise structural and compositional definition of Cu–BTA complexes very difficult, and emphasizes the need for new model compounds. We have therefore prepared a number of new benzotriazole compounds with copper and a few other metal ions. For comparison purposes, a few copper compounds containing N-methylbenzotriazole(Me-BTA) and 5-nitrobenzotriazole(NBTAH) are included.

Experimental

Starting Materials

Metal salts were used as the commercially available products, without further purification, unless otherwise indicated. Benzotriazole (Aldrich) and N-methylbenzotriazole (Riedel de Haen AG) were used without further purification. Organometallic compounds were prepared according to literature methods.

Synthesis of the Coordination Compounds

(BTA)(CuCl)

A solution of 1.02 g CuCl$_2$·2H$_2$O (6 mmol) in 15 ml ethanol was added with stirring to 1.67 g (14 mmol) benzotriazole in 30 ml ethanol. The thick green precipitate was collected on a filter, washed thoroughly with ethanol and dried *in vacuo* at 50 °C for 6 hr to give 1.06 g product. This material was insoluble in acetone or dimethyl sulfoxide, but dissolved in pyridine to give a green solution.

Cu$_2$(BTA)$_2$(BTAH)(NO$_3$)$_2$

A filtered solution of 1.45 g (6 mmol) Cu(NO$_3$)$_2$·3H$_2$O in 25 ml ethanol was added with stirring to 1.67 g (14 mmol) benzotriazole in 30 ml of the same solvent. The green solids were collected on a filter, washed with ethanol then ether, and dried *in vacuo* at 50 °C, yield 0.95 g.

(BTA)$_2$Cu

A solution of 0.6 g (2 mmol) copper(II) cyclohexanebutyrate [22] in 20 ml warm anhydrous

toluene was added with stirring to 0.48 g (4 mmol) benzotriazole in 25 ml dry toluene. The reaction mixture was stirred for 3 days under dry nitrogen. The green product was isolated by centrifugation, re-suspended in toluene and spun down again. After drying under high vacuum, the yield was 0.41 g. NMR analysis of the toluene filtrate showed that only cyclohexanebutyric acid was present. No carbonyl bands were observed in the IR spectrum of the Cu complex. The complex was insoluble in dimethylformamide or dimethyl sulfoxide; a yellow pyridine solution turned green on standing and deposited a green precipitate.

(BTA)$_3$Cu$_2$(BF$_4$)

A filtered solution of 0.9 g (3 mmol) anhydrous Cu(BF$_4$)$_2$ in 25 ml absolute ethanol was added with stirring to 0.71 g (6 mmol) benzotriazole in the same solvent. The reaction mixture turned deep green. The turquoise solids which separated were isolated by centrifugation, washed with ethanol and vacuum dried *in vacuo* at 50 °C, yield 0.57 g.

Cu(BTAH)Br$_2$

Equimolar (0.01 mmol) solutions of BTAH and CuBr$_2$ in ethanol (25 ml) were mixed, followed by the addition of 50 ml of n-pentane. Stirring overnight yielded a red-brown powder, which was isolated by filtration and washed with ethanol and n-pentane. After drying *in vacuo*, the m.p. was 233–235 °C.

Cu(BTAH)$_2$Cl$_2$·(H$_2$O)$_{0.5}$

A solution of benzotriazole (0.03 mmol) in 25 ml of ethanol was added to a solution of CuCl$_2$(H$_2$O)$_2$ (0.01 mmol) in 25 ml of ethanol and 3 ml of triethyl orthoformate. After addition of n-pentane (50 ml) and stirring for a few hours, green microcrystals separated, which were isolated by filtration, washed with ethanol and n-pentane and dried *in vacuo* (m.p. 235–236 °C). Without the addition of triethylorthoformate, this compound could not be isolated in a pure form. Nevertheless, about 0.5 mol of H$_2$O appeared to be present.

Cu(BTAH)$_3$Cl$_2$(H$_2$O)

A solution of benzotriazole (0.04 mmol) in 30 ml of ethanol was added to a solution of CuCl$_2$(H$_2$O)$_2$ (0.01 mmol) in 25 ml of ethanol. After addition of 50 ml of n-pentane and stirring overnight, a blue-green powder separated, which was isolated by filtration, washed with ethanol and n-pentane and dried *in vacuo* at room temperature. The compound initially was correctly analysed as Cu(BTAH)$_3$Cl$_2$(H$_2$O)-(EtOH), but appeared to lose ethanol upon standing in air. The melting point was 221–222 °C. Upon further standing in air for several weeks the colour changed from blue to deep green; the resulting solid analysed as Cu(BTAH)$_3$Cl$_2$.

$Cu(BTAH)_3Br_2(H_2O)_{0.25}$

Following the same procedure as described for the corresponding chloride, initially a product analysing as $Cu(BTAH)_3Br_2(H_2O)(EtOH)$ was formed. Upon standing in air the product converts from green to light brown (m.p. 188–189 °C), with apparent loss of ethanol and some of the water. In carrying out the reaction in methanol as a solvent, initially Cu-$(BTAH)_3Br_2(MeOH)(H_2O)$ was formed (green), which also was converted to the light brown product described above.

$Cu(BTAH)Cl_2$

Equimolar solutions of BTAH and $CuCl_2(H_2O)_2$ in ethanol (25 ml) were mixed, after which an excess (50–100 ml) of n-pentane was added. Stirring overnight yielded a yellow-brown powder (m.p. above 300 °C), which was isolated by filtration, washed with ethanol and n-pentane, and finally dried *in vacuo*.

$(BTA)_2Cu_2(SO_4)BTAH$

Copper sulfate pentahydrate (0.5 g, 2 mmol) was dissolved in 30 ml 1:1 water ethanol. This was filtered into a stirred solution of 0.48 g (4 mmol) benzotriazole in 50 ml of the same solvent. The dull green precipitate was isolated by centrifugation, washed with ethanol and dried *in vacuo* at 50 °C, yield 0.6 g.

$Cu(NBTAH)_2Cl_2$

A hot solution of 0.01 mol of 5-nitrobenzotriazole in ethanol (100 ml) was added to 0.004 mol of $CuCl_2$ in 10 ml of ethanol. After addition of n-pentane and stirring for two days, a green product was formed which was isolated by filtration, washed with ethanol and n-pentane, and dried *in vacuo*. The melting point appeared to be higher than 300 °C.

$Cu(NBTAH)_2Br_2$

A similar procedure as described for the chloride, yielded a yellow powder (m.p. 250–251 °C).

$Cu(MeBTA)Cl_2$

A solution of 0.01 mol of N-methylbenzotriazole in ethanol was added to a solution of 0.01 mol of $CuCl_2(H_2O)_2$ in 10 ml of ethanol. After addition of n-pentane and stirring overnight, a yellow-brown powder was isolated by filtration. After washing with ethanol and drying *in vacuo*, the melting point was 259–262 °C.

$Cu(MeBTA)_2Cl_2$

In a similar procedure as described for Cu(Me-BTA)Cl_2, but using 0.02 mol of MeBTA, a blue-green microcrystalline material (m.p. 208–209 °C) was isolated.

$Cu(MeBTA)Br_2$

In a procedure similar to that described for the corresponding chloride, a black product was isolated (m.p. 205–206 °C).

$Cu(MeBTA)_2Br_2$

In a procedure similar to that described for the corresponding chloride, a dark brown-green product (m.p. 211–212 °C) was isolated.

$[(BTA)Ni(BTAH)]BF_4$

Benzotriazole (0.67 g, 5.6 mmol) and triethylamine (0.5 g) in 10 ml tetrahydrofuran were added to a suspension of 1.7 g (5.6 mmol) $[CpNi(C_7H_8)]$-BF_4 [25] in 25 ml THF. After 24 hr, the reaction mixture was filtered under nitrogen to give 1.4 g of product as a light brown solid.

$CH_3Hg(BTA)$

To a filtered solution of 2.75 g (10 mmol) methylmercuric acetate in 50 ml warm acetone was added 1.19 g (10 mmol) benzotriazole followed by 1.01 g (10 mmol) triethylamine. The crystals which separated during four hours were collected on a filter and dried, yield 1.91 g. A 1.7 g sample was recrystallised from hot acetonitrile to provide 1.2 g of pure product, m.p. 190–192 °C. Electronic spectrum (CH_3OH): 260 (log $\epsilon = 2.76$), 276(3.72) nm. The mass spectrum showed ions due to Hg^+ and $HgCH_3^+$. ^1H NMR (dmso-d_6): A_2B_2 pattern centered at 7.53 ppm; 0.88 ppm (s, J_{Hg-C-H} 212 cps). Molar conductivity (1.37×10^{-3} M in nitromethane): 1.2 ohm^{-1} cm^2 mol^{-1}.

$(BTAH)_2PdCl_2$

To a solution of 1.15 g $(PhCN)_2PdCl_2$ (3 mmol) in 100 ml warm acetonitrile was added 0.72 g (6 mmol) benzotriazole in 25 ml of the same solvent. After 30 min the yellow microcrystalline product was filtered off, washed with fresh solvent, and dried under vacuum, yield 1.02 g. Electronic spectrum (Nujol): λ_{max} at 280,295(sh) nm. A 0.5 g sample was recrystallised from aqueous dimethyl sulfoxide to produce 0.23 g of $(BTAH)_2PdCl_2(dmso)_2$ as yellow needles. Electronic spectrum (Nujol): 280,330-(sh) nm.

$(BTAH)HgCl_2$

Mercuric chloride (1.35 g, 5 mmol) and 1.19 g (10 mmol) benzotriazole, each in 25 ml ethanol, were combined. After standing overnight, the reaction mixture was filtered to afford, after washing with ethanol, 1.65 g of product. This was recrystallized from acetone–chloroform to give 1.4 g of the pure compound. ^1H NMR (dmso-d_6): A_2B_2 pattern centered at 7.75 ppm. Electronic spectrum (C_2H_5OH): λ_{max} at 260(3.11) nm. The mass spectrum showed peaks due to benzotriazole, $HgCl_2^+$, $HgCl^+$ and Hg^+.

(BTAH)₂ZnCl₂

A solution of 1.36 g zinc chloride (10 mmol) in 20 ml ethanol, was filtered to remove insoluble material and added to 2.4 g (20 mmol) benzotriazole in 10 ml ethanol. After 20 hr the product was filtered off and air dried. It was then dissolved in 75 ml warm acetone. The solution was centrifuged to remove some insoluble impurities and reduced under vacuum to about 10 ml to give 1.6 g of white microcrystals. Electronic spectrum (Nujol): λ_{max} at 280,320(sh) and 360 nm. ^{1}H NMR (dmso(-d₆): A_2B_2 pattern at 7.75 ppm (4H); 12.2 ppm (br, s, 1H).

(BTAH)CdCl₂

Cadmium chloride (10 mmol) in 30 ml 2:1 ethanol—water was filtered into a solution of 20 mmol (2.4 g) benzotriazole in 15 ml of the same solvent. Filtration gave 6.1 g of white product. This was dissolved in 70 ml warm dimethyl sulfoxide. The solution was diluted with water to the cloud point. On standing, a gelatinous precipitate and white nodules consisting of bunches of needles separated. The former was removed by decantation and by repeated washing with aqueous ethanol. The remaining crystals, after drying *in vacuo* at 50 °C, weighed 0.8 g. The recrystallisation did not cause any change in the infrared spectrum. Electronic spectrum (Nujol): λ_{max} at 280,340(sh) nm.

(BTA)₂Hg

A solution of 2.26 g (5 mmol) Hg(ClO₄)₂·3H₂O in 20 ml ethanol and a solution of 1.2 g (10 mmol) benzotriazole and 1.4 ml triethylamine in 10 ml ethanol were combined. The white product was collected on a filter, washed with ethanol then ether, and vacuum dried, yield 1.7 g. An analytical sample was obtained by crystallisation from pyridine—water, yield 0.7 g. Electronic spectrum (Nujol): λ_{max} at 275,240(sh) nm.

(BTAH)₂TiCl₄

A solution of titanium tetrachloride (5 mmol) in 15 ml dichloromethane was treated with 1.2 g (10 mmol) benzotriazole. The orange product was filtered off, washed with more dichloromethane and dried under vacuum, yield 1.62 g. The material was moisture-sensitive and turned white on exposure to air.

(BTA)SiMe₃

Lithium benzotriazolate was prepared from 60 mmol butyllithium and 60 mmol (7.14 g) benzotriazole in 150 ml ethylether. This was cooled in an ice bath and 60 mmol trimethylsilyl chloride in 10 ml ether added with stirring. The mixture was stirred under gentle reflux for 8 hr, then filtered and the solvent removed under reduced pressure. Distillation of the residue through a 6″ Vigreux column afforded 9.1 g of product as a colorless moisture-sensitive liquid, b.p. 81–83°/15μ. The mass spectra at 15 and 70 eV did not reveal a parent ion; at 70 eV, a strong peak at m/e 148 attributed to loss of N₂ and CH₃ from M⁺ was observed; the relative intensities of m/e 149 ($^{13}C^{12}C_7{}^1H_{10}{}^{14}N^{28}Si$) and m/e 150 ($^{12}C_8{}^1H_{10}{}^{14}N^{30}Si$) were 8 (Calc. 6) and 3 (Calc. 2) respectively. ^{1}H NMR (toluene-d₈): complex multiplet in aromatic region (4H), singlet at 0.0 ppm (1H, J_{C-H} 43, $^3J_{Si-C-H}$ 18). The spectrum was unchanged at 110 °C.

SnCl₄(BTAH)₂

A solution of 1.3 g (5 mmol) stannic chloride in 5 ml dry dichloromethane was added with vigorous stirring to 1.2 g (10 mmol) benzotriazole in 15 ml of the same solvent. The product separated and was collected on a filter, washed with dichloromethane and dried under vacuum, yield 2.4 g. It was stored under dry nitrogen.

[(Phenanthroline)₂Cu(BTA)₂]

A mixture of 0.5 g (1 mmol) [(phenanthroline)₂-Cu]BF₄)₂, 0.24 g (2 mmol) benzotriazole and 10 ml acetonitrile was stirred for 5 min. To this blue mixture was added 2 mmol (0.2 g) triethylamine whereupon the color turned green and the remaining solids dissolved. After standing overnight, the hemispherical green nodules were filtered, washed with acetonitrile then diethyl ether, and vacuum dried, yield 0.15 g.

(BTA)Mn(CO)₅

A solution of LiBTA was prepared by adding 4 mmol of n-butyllithium in hexane to 0.48 g (4 mmol) benzotriazole in 20 ml dry tetrahydrofuran. A solution of 1.18 g (4 mmol) resublimed BrMn(CO)₅ in 15 ml THF was subsequently added. After stirring for 8 hr, the solvents were removed under vacuum and the residue extracted with toluene. Addition of hexane to the extract produced, the yellow microcrystalline product which separated was dried under high vacuum, yield 0.25 g. ^{1}H NMR (CD₃CN): unsymmetrical multiplet centered at 7.3 ppm.

Analyses

Metal analyses were carried out by standard procedures, mainly based upon complexometric titrations [27]. Carbon, hydrogen, nitrogen, chlorine, bromine, fluorine, and sulphur were determined by commercial laboratories.

Spectroscopic and Magnetic Data

Infrared spectra were recorded as Nujol mulls and KBr discs on Perkin Elmer and Beckman spectrometers. Far-infrared spectra were obtained as pressed polythene discs (450–50 cm⁻¹) on a Beckman far-IR FS-720 interferometer.

Ligand-field spectra were obtained by diffuse reflectance and in some cases as Nujol mull on a Beckmann DK-2A instrument (35,000–5000 cm^{-1}).

ESR spectra were recorded on a Varian E4 instrument operating at X-band frequencies. A few spectra were also investigated using Q-band operation. The spectra were obtained on powders at room temperature.

^{1}H NMR spectra were obtained at 60 MHz on a Varian T-60 spectrometer.

Mass spectra were obtained in the electron impact mode using, unless otherwise indicated, 70 eV electrons.

Conductivity measurements were made with a commercially available glass apparatus having a ceil constant of 0.136 cm^{-1}.

Results

General

All compounds are listed in Table I, together with their colours and analytical data. The infrared spectra

of the compounds are tabulated in Table II. Far-IR spectra of some of the compounds are given in Table III, together with tentative assignments of M–X and M–N vibrations. Ligand-field and EPR spectra are summarised in Table IV. Results of other physical and analytical studies of some compounds are mentioned under the experimental section.

The compounds and their possible structures will be discussed on the basis of a combination of all spectral and magnetic studies.

Copper–Benzotriazole Compounds

Copper(II) complexes of benzotriazole may be easily prepared by the reaction of *1* in ethanol with various copper salts. These systems are, however, quite complex. The products obtained are green, polymeric, amorphous powders whose stoichiometries depend on the counter ion in the starting copper salt. Thus, [(BTA)CuCl], *2* is formed on mixing ethanolic solutions of *1* and CuCl$_2$·2H$_2$O, while the analogous material prepared from Cu(NO$_3$)·2H$_2$O has an elemental analysis which

TABLE I. Benzotriazole Coordination Compounds: Colours and Analytical Data.

Compounds	No.	%Metal		%Carbon		%Nitrogen		%Hydrogen		%Anion		Colour
		fnd.	calcd.	fnd.	calcd.	fnd.	calcd.	fnd.	calcd.	fnd.	calcd.	
Cu(BTA)Cl	2	30.1	29.5	33.4	33.2	19.6	19.4	2.0	1.8	16.1	16.1	green
Cu$_2$(BTA)$_2$(BTAH)(NO$_3$)$_2$	3	20.1	20.9	35.9	35.5	25.3	25.3	2.8	2.5			green
Cu$_2$(BTA)$_2$(BTAH)SO$_4$	4	23.0	22.0	36.0	37.4	21.7	21.9	2.9	2.3	5.0	5.5^a	dull green
Cu$_2$(BTA)$_3$(BF$_4$)	5	21.6	22.4	38.6	38.0	22.1	22.2	2.9	2.1	12.8	13.4^b	blue green
Cu(BTA)$_2$	6	20.7	21.3	48.3	48.0	28.1	28.0	3.2	2.7			green
Cu(BTAH)Cl$_2$	7	24.9	25.0	28.8	28.4	16.3	16.6	1.8	2.0	27.2	28.0	yellow brown
Cu(BTAH)$_2$Cl$_2$(H$_2$O)$_{0.5}$	8	16.3	16.5	38.7	37.9	22.1	22.0	2.9	2.9	18.7	18.6	green
Cu(BTAH)$_3$Cl$_2$(H$_2$O)	9	12.5	12.4	42.7	42.4	24.6	24.7	3.6	3.4	14.2	13.9	blue green
Cu(BTAH)Br$_2$	10	18.5	18.5	21.3	21.1	12.2	12.3	1.6	1.5	45.6	46.6	red brown
Cu(BTAH)$_3$Br$_2$(H$_2$O)$_{0.25}$	11	10.9	10.9	36.0	36.9	20.6	21.5	2.6	2.7	24.5	24.8	light brown
Cu(BTA)$_2$(phen)$_2$	12	13.6	13.3	59.7	60.0	23.4	23.3	3.3	3.3			green
Zn(BTAH)$_2$Cl$_2$	13	17.9	17.4	38.0	38.5	22.1	22.5	2.4	2.7	18.9	19.0	white
Cd(BTAH)Cl$_2$	14	37.5	37.1	24.2	23.8	14.1	14.0	1.7	1.7	23.3	23.5	white
Hg(BTAH)Cl$_2$	15	50.9	51.5	18.5	18.4	10.5	10.7	1.3	1.3	18.6	18.2	white
Ti(BTAH)$_2$Cl$_4$	16	10.7	11.2	33.9	33.6	19.7	19.6	2.9	2.3	33.8	33.2	orange
Sn(BTAH)$_2$Cl$_4$	17	24.8	25.1	25.2	25.3	18.4	17.7	2.1	2.1	39.1	29.9	white
Pd(BTAH)$_2$Cl$_2$	18	25.9	25.5	34.4	34.7	20.4	20.2	2.5	2.4	17.1	17.1	yellow
Pd(BTAH)$_2$Cl$_2$(dmso)$_2$	19	19.2	18.6	33.3	33.6	14.1	14.7	3.8	3.9	12.7	12.4^c	yellow
Hg(BTA)$_2$	20	45.4	46.0	33.1	33.0	19.0	19.2	2.3	1.8			white
Hg(BTA)(CH$_3$)	21	60.1	60.2	25.0	25.2	12.3	12.6	2.3	2.1			white
Si(BTA)(CH$_3$)$_3$	22			56.4	56.3	21.9	21.9	6.7	6.8			colourless
Mn(BTA)(CO)$_5$	23	17.8	17.6	42.6	42.2	13.7	13.4	1.8	1.3			yellow
Ni(BTA)(BTAH)BF$_4$	24	16.4	15.4	37.7	37.6	20.3	21.9	2.5	2.4			light brown
Cu(NBTAH)$_2$Cl$_2$	25	13.3	13.7	31.3	31.2	23.9	24.2	1.9	1.7	15.5	15.3	green
Cu(NBTAH)$_2$Br$_2$	26	12.7	11.5	25.8	26.1	20.0	20.3	1.5	1.5	28.9	29.0	yellow
Cu(MeBTA)Cl$_2$	27	23.8	23.7	31.7	31.4	15.7	15.7	2.7	2.6	26.6	26.5	yellow brown
Cu(MeBTA)$_2$Cl$_2$	28	15.8	15.8	41.8	41.9	20.8	21.0	3.6	3.5	17.9	17.7	blue green
Cu(MeBTA)Br$_2$	29	18.1	17.8	23.7	23.6	11.8	11.8	2.1	2.0	44.6	44.8	black
Cu(MeBTA)$_2$Br$_2$	30	13.3	13.0	34.4	34.3	17.1	17.2	3.0	2.9	32.4	32.6	green brown
Cu(BTAH)$_3$Cl$_2$	31	13.1	13.0	43.3	43.9	25.2	25.6	3.0	3.1	14.9	14.4	deep green

^{a}%S. ^{b}%F. ^{c}%S 11.8 (calcd. 11.2).

TABLE II. Infrared Spectral Data (4000–500 cm^{-1}) of (Substituted) Benzotriazole Compounds.

Compound		Absorption (cm^{-1})
BTAH	1	3145m,3065m,2990m,2790s,2710s,2360msh,1621m,1594m,1578w,1561w,1542w,1490w, 1457m,1420m,1384m,1308m,1280m,1268m,1211vs,1185msh,1146m,1123m,1118m, 1077m,1024s,1015s,980m,908m,898m,879m,780s,772m,754vs,737vs,705m
Cu(BTA)Cl	2	3075w,1615w,1595w,1580m,1300w,1275s,1220s,1150w,1025m,995w,790s,745s,640m, 560m
$Cu_2(BTA)_2(BTAH)(NO_3)_2$	3	3100w,2950m,2920m,2850m,1550m,1475s,1445s,1290s,1275s,1215s,1150w,1025s,790s, 745s,685w,640m,560m
$Cu_2(BTA)_2(BTAH)SO_4$	4	3350br,w,3190w,1675m,1290w,1265m,1200s,1140w,1115s,1030m,790s,745s,640m,555w
$Cu_2(BTA)_3BF_4$	5	1620s,1595m,1575m,1290m,1270s,1215s,1050s,790s,750s,635m,560m,520w
$Cu(BTA)_2$	6	1575m,1510m,1490m,1290m,1255s,1200s,990w,935w,920w,790s,740s,685w,635m,560m
$Cu(BTAH)Cl_2$	7	3170vs,3120msh,3000msh,2900msh,1620m,1596m,1454m,1416m,1402s,1323w,1302m, 1285m,1280m,1225s,1164w,1120s,1041s,997w,952w,851w,780s,761m,740vs
$Cu_2(BTAH)_4Cl_4 \cdot H_2O$	8	3145vs,3100vs,3000ssh,2905s,2865ssh,2805s,2710m,2530msh,2440msh,1623m,1597m, 1457m,1418m,1407m,1313w,1304w,1288m,1282m,1225s,1154w,1122s,1041s,1034msh, 782m,762msh,742ssh,735vs
$Cu(BTAH)_3Cl_2(H_2O)$	9	3250mbr,3095m,2970m,2860m,2790m,1597m,1454w,1446m,1398m,1301w,1280m, 1216sbr,1142w,1124w,1111m,1038m,1024msh,1011m,997m,907m,788msh,780m,768m, 742vs,732vs,699m
$Cu(BTAH)Br_2$	10	3300vs,3175m,1617w,1596m,1501w,1453m,1392m,1306m,1285m,1274m,1230s,1163w, 1113s,1036s,1000w,973w,955w,847w,779m,763m,740vs,701vs
$Cu(BTAH)_3Br_2(H_2O)_{0.25}$	11	3170s,3120msh,3000msh,2560m,1620m,1599m,1454m,1443msh,1386s,1304msh,1292m, 1278m,1275msh,1219s,1144m,1116m,1039m,1033m,1016m,946w,898w,797m,779m, 768m,747s,737s,725msh
$Cu(BTA)_2(phen)_2$	12	1585m,1575m,1445m,1425m,1345w,1280w,1190m,1175m,1150s,1120s,1115m,1080s, 990w,870s,850s,780s,775s,740s,720s,680w,550w
$Zn(BTAH)_2Cl_2$	13	3100sbr,1600m,1380m,1290s,1275s,1220s,1120s,1035s,990m,910s,775s,755s,745s
$Cd(BTAH)Cl_2$	14	3220s,1620w,1600m,1295m,1270s,1225s,1215msh,1100s,1030s,905w,780s,765w,740s, 650m,560w
$Hg(BTAH)Cl_2$	15	3275s,1640m,1615m,1290w,1275w,1260s,1220s,1090s,1020s,905m,775s,755s,740s,645m
$Ti(BTAH)_2Cl_4$	16	3250sbr,1590m,1270s,1230s,1214s,1120s,1030s,910m,775m,745s,695w,540w
$Sn(BTAH)_2Cl_4$	17	3260sbr,1590m,1280s,1240s,1125s,1035s,910s,780s,760m,750s,725s,650w,635w,540w
$Pd(BTAH)_2Cl_2$	18	3170sbr,1600m,1305m,1230s,1125s,1045s,910m,780s,760m,745s,720s,645m,635m,545w
$Pd(BTAH)_2Cl_2(dmso)_2$	19	3170,1600m,1310m,1275m,1225s,1140w,1040w,1020sbr,955m,905m,780s,750s,640w, 550w
$Hg(BTA)_2$	20	3180w,1600m,1575m,1480m,1280m,1260s,1210m,1195s,1175s,1155s,1140m,1120w, 1095m,990m,920m,775s,740s,670w,640m,545m
$Hg(BTA)CH_3$	21	1450m,1280m,1195s,1125s,1100s,990m,940w,910m,795m,780s,765w,740s,675w,635m, 610m,595m
$Si(BTA)(CH_3)_3$	22	3060w,2960m,2900m,1610m,1450s,1435s,1325s,1275s,1255s,1240m,1150s,1125m,1015s, 995s,915s,845sbr,780s,760m,745s,655s,625m,550s
$Mn(BTA)(CO)_5$	23	3150w,2100m,2030s,1925s,1580w,1260m,1180s,1150m,1045m,780s,740s,690s,635s, 560w,520m
$Ni(BTA)(BTAH)BF_4$	24	3050s,1630w,1290m,1265s,1210s,1150m,1060vs,920w,790s,750s,695m,645m,560m,530w
$Cu(NBTAH)_2Cl_2$	25	3070vs,1625m,1600m,1553s,1536m,1403m,1397m,1351s,1221s,888s,800s
$Cu(NBTAH)_2Br_2$	26	3200vs,3120s,1625m,1598w,1551m,1534m,1400w,1383w,1350vs,1221m,885s,800s
$Cu(MeBTA)Cl_2$	27	1611w,1590m,1461m,1428w,1390w,1224s,781s,742s
$Cu(MeBTA)_2Cl_2$	28	1607w,1591m,1458m,1432w,1388w,1225s,781s,775m,768s,757s,740s
$Cu(MeBTA)Br_2$	29	1607w,1588m,1456m,1419w,1388w,1218s,778s,744s,735m
$Cu(MeBTA)_2Br_2$	30	1605w,1590m,1455m,1421w,1386w,1220s,778s,769m,763s,748s,737s
$Cu(BTAH)_3Cl_2$	31	3470mbr,?160msh,3130msh,3050s,2980s,2870m,2805s,2735s,1627w,1600m,1482w, 1458w,1440m,1311m,1305m,1291m,1280m,1224s,1146m,1129m,1082m,1035s,877m, 781s,771m,755ssh,744vs

ᵃOnly the most important bands are listed; many weak and very weak bands have been omitted. s = strong; m = medium; w = weak; v = very; sh = shoulder.

TABLE III. Far-IR Spectra (500–100 cm^{-1}) of Some BTA, BTAH, NBTAH and MeBTA Compounds.[a]

Compound	No.	M–Cl bands	M–Br bands	M–N bands	Other Vibrations
Cu(BTAH)Cl$_2$	7	310vs,285vs,194s		297s	439s,428s,248s,161m,144m,135s
Cu(BTAH)Br$_2$	10		232vs,124s	298s	435s,428s,248s,184m,148m,137m
Cu$_2$(BTAH)$_4$Cl$_4$(H$_2$O)	8	307vs,194vs		296vs	442s,426s,255s,182m,148m
Cu(BTAH)$_3$Cl$_2$(H$_2$O)	9	297vs,195m		310s	442s,434s,425s,276m,248m,242m,185m, 177m,162m,155m
Cu(BTAH)$_3$Cl$_2$	31	300vs		316s	255m,vbr
Cu(BTAH)$_3$Br$_2$(H$_2$O)$_{0.25}$	11		233s,142s	322s	446s,440m,432s,271s,240m,194m,156m
Cu(NBTAH)$_2$Cl$_2$	25	304vs,200s		272m	443s,430s,356s,332s,264s,237m,132s
Cu(NBTAH)$_2$Br$_2$	26		246s,231s	274s	443s,428s,354s,333vs,259m,139s,120s
Cu(MeBTA)$_2$Cl$_2$	28	299vs,179s		272s,265s	434s,248s,237s,171vs,163vs
Cu(MeBTA)$_2$Br$_2$	30		250s	287s,263vs	434s,242s,234s,171s,167m,112m
Cu(MeBTA)Br$_2$	29		225m,192vs	268m	433s,240m,180s,153s
Cu(MeBTA)Cl$_2$	27	298vs,197s		290s	428s,249s,236s,175s,169s,158vs
Zn(BTAH)$_2$Cl$_2$	13	305s,295s		280sh	425s
Ti(BTAH)$_2$Cl$_4$	16	375s,355s			
Hg(BTAH)Cl$_2$	15	325s,280m			435s,420m,110w

[a]Assignments are based upon mutual comparison of chlorides and bromides and upon literature assignments [28, 31].

TABLE IV. Ligand-field and EPR Spectra of Some Copper BTA, BTAH, NBTAH and MeBTA Compounds.

Compound	No.	Ligand-field maxima[a] (kK)	E.P.R. Powder Values[b]		
			g_{iso}	$g_∥$	$g_⊥$
Cu$_2$(BTA)$_3$BF$_4$	5	14.5	2.14		
Cu(BTA)$_2$	6	14.0		2.24	2.06
Cu(BTAH)Cl$_2$	7	13.1		2.27	2.12
Cu$_2$(BTAH)$_4$Cl$_4$(H$_2$O)	8	13.8		2.03	2.16 2.20[c]
Cu(BTAH)$_3$Cl$_2$(H$_2$O)	9	13.5		2.29	2.08 2.04
Cu(BTAH)$_3$Cl$_2$	31	14.0		2.16	2.04
Cu(BTAH)Br$_2$	10	12.8	2.14br		
Cu(BTAH)$_3$Br$_2$(H$_2$O)$_{0.25}$	11	12.5		2.01	2.13 2.21[c]
Cu(MeBTA)$_2$Br$_2$	30	14.8		2.22	2.07
Cu(MeBTA)$_2$Cl$_2$	28	14.3 12.1sh		2.22	2.10
Cu(NBTAH)$_2$Cl$_2$	25	13.9		2.04	2.16 2.20[c]
Cu(NBTAH)$_2$Br$_2$	26	14.1	2.15		
Cu(MeBTA)Cl$_2$	27	14.3 8.7sh	2.14		
Cu(MeBTA)Br$_2$	29	black		2.22	2.07
Cu(BTA)Cl	2	13.4 10.0sh	2.12		
Cu(BTA)$_2$(phen)$_2$	12	15.8 12.0sh		2.23	2.06
Cu$_2$(BTA)$_2$(BTAH)(NO$_3$)$_2$	3	15.9 10.0sh	2.12		
Cu$_2$(BTA)$_2$(BTAH)(SO$_4$)	4	15.2 9.5sh	2.09vbr		

[a]Recorded as diffuse reflectance spectra. [b]EPR data as listed are obtained from powders at room temperature, using X-band frequencies; Q-band spectra give different parameters in many cases. [c]These spectra have a d$_{z^2}$ ground state for the Cu(II) ion; no indications for zero-field splitting due to the dimers (known to be present for compound 8 [23]) are observed.

corresponds to [(BTA)Cu(NO$_3$)$_2$(BTAH)], 3. Using CuSO$_4$·H$_2$O and Cu(BF$_4$)$_2$ as starting materials, (BTA)Cu$_2$SO$_4$(BTAH), 4 and (BTA)$_3$Cu$_2$BF$_4$, 5, respectively were obtained. Pure cupric bis(benzotriazole), Cu(BTA)$_2$, 6, was obtained from 1 and copper(II) cyclohexylbutyrate in toluene. Use of a copper(II) derivative containing a weakly nucleophilic anion and a solvent of low polarity appears to be necessary to obtain a compound free of coordinated

counter ions and 1. Another anion-free material, (phenanthroline)$_2$Cu(BTA)$_2$, 12, was synthesized from 1, triethylamine, and [(phenantroline)$_2$Cu]-(BF$_4$)$_2$. In view of the preference of Cu(II) for a coordination number of six, this compound most likely has an octahedral coordination geometry comprised of two bidentate phenanthroline molecules and two monodentate benzotrizolato ligands. It is unfortunate that the solubility of the twinned

crystals was too low to obtain a solution-phase EPR spectrum.

The infrared spectrum of the benzotriazole–copper nitrate complex, *3*, shows bands at 1025, 1290 and 1445 cm^{-1} which is suggestive of a bidentate NO_3 group. The sulfate ion in *4* also appears to be bidentate; infrared bands at 1030, 1115 and 1140 cm^{-1} are assigned to the S–O ν_3 mode and at 600 and 640 cm^{-1} to the ν_4 mode in the complexed anion. Using the mixed solvent system ethanol/n-pentane yielded species of formula $Cu(BTAH)_n X_2$, with n = 1, 2 and 3. In case of n = 1, both the chloride and the bromide could be isolated, (*7* and *10*). The far-IR spectra of these compounds show both terminal and bridging Cu–Cl vibrations (Table III) in addition to the Cu–N vibrations. Assignments in Table III are based on earlier work ([28] and references cited therein) with imidazoles, pyrazoles and pyridines as N-donor ligands. The ligand field spectra of these compounds, and the other copper compounds reported below, show maxima in the range 12.5–15.9 kK, which is in agreement with octahedral coordination geometry. In the case of n = 2, only the chloride could be isolated as a hemi hydrate, *8*. The spectral data suggest a similar structure as suggested for the mono BTAH species, having monodentate coordination of BTAH.

Far-IR, UV–Vis and EPR spectra resemble those of other compounds $Cu(azole)_2 X_2$ for which halogen-bridged linear-chain structures or dimeric halogen-bridged structures are known [29]. The recently determined X-ray structure [24] of $[CuCl_2(BTAH)_2]_2 \cdot H_2O$ confirms this picture. In the case of n = 3, $Cu(BTAH)_3 X_2(EtOH)(H_2O)$ species are initially isolated, which easily lose EtOH upon standing in the air or slight drying *in vacuo*. The high values for the ν(Cu–N) stretching frequency (310–322 cm^{-1}) suggest monodentate BTAH coordination. It is not clear whether or not the water molecules are coordinated. In the latter case they can be expected to be involved in a hydrogen bonding network with the BTAH ligand and/or the halide anions.

Upon standing for several months, the ethanol adduct of *9* slowly loses all its water and EtOH and converts into compound *31*, with completely different spectral properties (as can be seen from Tables III and IV). The most likely explanation for this is a structural change, in which the BTAH ligands are converted from monodentate to bidentate, at least for part of the BTAH.

The EPR spectra listed in Table IV all show either isotropic g values or indications for axial or rhombic splittings. In no case are copper hyperfine splittings observed. This indicates that the copper ions in the solid compounds are exchange coupled. The order of magnitude of this coupling must be at least the size of the hyperfine coupling constants for ^{63}Cu and ^{65}Cu. The fact that the observed g values at X-band frequency differ from those obtained at Q-band frequency also indicates the occurrence of magnetic exchange coupling [30]. No attempts were undertaken to investigate the precise J values from susceptibility measurements at low temperature. The known dimeric compound *8* does not show the lines characteristic for S = 1 Cu^{II} dimers [30]. This might be related to the fact that the unit cell contains two crystallographically independent dimers [24] and that coupling occurs between the dimers through the crystal lattice via hydrogen bonding. Very recently, Hodgson and Pedersen [38] have shown that the magnetic exchange in this dimer is ferromagnetic (J = +1 cm^{-1}). The interdimer exchange (J') was found to be very small, however.

Benzotriazole Compounds with Other Metal Salts

Benzotriazole forms adducts with a wide variety of metal halides. From the reaction with zinc chloride, $(BTAH)_2 ZnCl_2$, *13*, was isolated. It exhibits an infrared band at 300 cm^{-1} due to Zn–Cl stretching and so the complex presumably has the tetrahedral geometry usual for Zn(II). This structure was recently proven by an X-ray analysis [24]. The chlorides of the heavier metals cadmium and mercury produce only 1:1 adducts $(BTAH)CdCl_2$, *14*, and $(BTAH)HgCl_2$, *15*, with benzotriazole. These are most likely chloride bridged species; in dimethyl sulfoxide, they dissociate to give free benzotriazole. Titanium tetrachloride afforded orange, moisture sensitive $(BTAH)_2 TiCl_4$, *16*. The infrared spectrum of this compound showed bands at 375 and 355 cm^{-1}, indicative of a *trans* octahedral structure [31]. A similar geometry is proposed for the tin analogue, $(BTAH)_2 SnCl_4$, *17*.

Benzotriazole displaces benzonitrile from $(PhCN)_2 PdCl_2$ to form $(BTAH)_2 PdCl_2$, *18*. A *cis* stereochemistry is indicated by far infrared absorptions at 370 and 320 cm^{-1}, assigned to Pd–Cl stretching vibrations. Recrystallization of this compound from dimethyl sulfoxide afforded $(BTAH)_2 PdCl_2(dmso)_2$, *19*. This new compound exhibited ν_{SO} at 1030 cm^{-1}, close to the value for free dimethyl sulfoxide, and no new bands in the 400–500 cm^{-1} range due to metal–oxygen stretching [32]. The broad, strong band at 3170 cm^{-1} in $(BTAH)_2 PdCl_2$, *18* is not present in the dmso complex, suggesting that the dmso is hydrogen bonded to the benzotriazole and not coordinated to palladium.

Reaction with salts containing weakly coordinating anions such as perchlorate leads, as in the example with Cu(II) cyclohexanebutyrate, to deprotonation and formation of a metal benzotriazolate. Thus, mercury(II) benzotriazolate *20* was obtained from benzotriazole and mercuric perchlorate in ethanol. Unlike the Cu(II) analogue, which is thought to be a crosslinked polymer, the mercury derivative could be recrystallized from aqueous pyridine. In the

conjugate base of benzotriazole, the existence of two resonance forms A and B (Fig. 1) implies averaging of N—N double and single bonds. The reduced N—N bond order is reflected in a lowered N—N stretching frequency in salts and ionic benzotriazole derivatives. Thus, this band occurs at 1220—1240 cm⁻¹ in neutral complexes and at 1085 cm⁻¹ in thallium benzotriazolate. The corresponding band in $(C_6H_4N_3)_2Hg$ is a structured absorption centered at 1155 cm⁻¹. On this basis it appears that mercury(II) benzotriazolate is at least partly ionic with coordination to all three nitrogens in the solid state.

Organometallic compounds of silicon, mercury and manganese were prepared in a search for materials which might exhibit η_3 bonding between the metal and the C_2N_3 ring. N-trimethylsilylbenzotriazole, *16*, prepared from lithiobenzotriazole and $(CH_3)_3SiCl$, displayed an asymmetrical multiplet in the ¹H NMR spectrum at room temperature which was unchanged up to 110 °C; this compound does not appear to be fluxional. Benzotriazolatomanganese pentacarbonyl, *23*, was similarly prepared from $BrMn(CO)_5$. It exhibited ν_{CO} at 2031 and 1937 cm⁻¹ and ν_{NN} at 1185 cm⁻¹. The pattern of metal carbonyl absorptions and the progressive loss of CO from the molecular ion in the mass spectrum show that this is a $LMn(CO)_5$ compound which must then contain monodentate benzotriazole. The compound decomposed on ultraviolet irradiation.

Triethylammonium benzotriazolate in tetrahydrofuran displaced both cycloheptatriene and the cyclopentadienyl ligand from $[CpNi(C_7H_8)]BF_4$ to form $[(BTA)Ni(BTAH)]BF_4$. The structure of this compound is difficult to deduce, although it seems that both BTA and BTAH are coordinated and bridging, resulting in a 4, 5 or 6 coordination for the nickel(II) ion.

Copper Halides Coordinated by Substituted Benzotriazoles

In the case of 5-nitro-benzotriazole an impure product approaching the formula $Cu(NBTA)_2$ was isolated but not investigated. Using the ethanol—pentane method, pure species $Cu(NBATH)_2X_2$ with X = Cl (*25*) and Br (*26*) were isolated. The spectral properties of these two compounds are very similar. Halogen-bridged linear-chain compounds with monodentate ligands are likely structures, according to ligand-field, EPR and far-IR spectra. Similar structures are proposed for the corresponding compounds containing N-MeBTA, *28* (X = Cl) and *30* (X = Br). With this latter ligand species $Cu(MeBTA)X_2$, *i.e.* *27* (X = Cl) and *29* (X = Br) are also formed. From the spectral data it cannot be deduced that the ligand is bidentate coordinated. Differences in the mid-IR region suggest a different binding mode compared to that in compounds *28* and *30*.

Discussion

From the results presented above it is clear that benzotriazole is a versatile ligand, giving rise to both protonated (BTAH) and deprotonated (BTA⁻) ligands. The coordination to metal ions can be monodentate (using N(1) in BTA and using N(3) in BTAH), bidentate (using either two adjacent N-atoms, as found [17] in $Ni_3(BTA)_6$, or using N(1) and N(3) as found in the X-ray structure [18] of [(MNTB)Cu-(BTA)(NMTB)](NO₃)₃)]), or tridentate (as found in TlBTA [21]). Monodentate neutral BTAH, using N(3) coordination seems to be present in the compounds $M(BTAH)_2Cl_2$ (M = Zn, Pd), $M(BTAH)_3X_2$-$(H_2O)_n$ (M = Cu, n = 1, 0.25, X = Cl, Br), $M(BTAH)_2$-Cl_4 (M = Sn, Ti). This structure has been proven for $Zn(BTAH)_2Cl_2$ [23]. Such a monodentate coordination has also been found in the X-ray structure of $Co(1\text{-vinylbenzotriazole})_2Cl_2$ [33]. Similar structures can be proposed for $Cu(MeBTA)_2X_2$ and $Cu(NBTA-H)_2X_2$. Monodentate N(1) coordination in anionic BTA seems likely in $Cu(BTA)_2(phen)_2$, $Hg(BTA)CH_3$, $Si(BTA)(CH_3)_3$ and $Mn(BTA)(CO)_5$ just as found in the X-ray structure of $Ir(CO)(Ph_3P)_2(BTA)$ [20]. Bidentate neutral BTAH seems to be present in Cu-$(BTAH)X_2$, $Cu(BTAH)_3Cl_2$ (compound *31*), and possibly in $M(BTAH)Cl_2$ (M = Cd, Mg). Also in the mixed compounds with both BTAH and BTA ligands, bidentate neutral BTAH could occur. Further, $Cu(MeBTA)X_2$ compounds are proposed to contain bidentate bridging ligands (using N(2) and N(3) respectively). Bidentate (or possibly tridentate) bridging BTA⁻ is supposed to be present in compounds *2*, *3*, *4*, *5* and *6* and *24*. The insoluble nature of these products also points to this direction, but prevents further investigation.

Relationship to Surface Complexes and Concluding Remarks

Recent research in benzotriazole—metal chemistry allows a partial reconstruction of the events leading to the formation of passivating films on copper. Presumably, the first step is chemisorption of benzotriazole, either from the vapor or from solution, although surface-sensitive spectroscopic studies on atomically clean copper surfaces have yet to be reported. Subsequently, elimination of hydrogen generates cuprous benzotriazole. This product has been identified on copper by its characteristic emission spectrum and by X-ray photoelectron spectroscopy [21, 33, 34]. Such a reaction on a metal below hydrogen in the electromotive series is somewhat surprising. However, surface CH_3O—Cu and C_2H_5O—Cu species, formed on Cu(100) by loss of hydrogen from methanol and ethanol, have been detected by high resolution energy loss spectroscopy [35]. It is

possible that oxygen on the surface of the copper acts as a base to deprotonate benzotriazole, since it is known [36,37] that chemisorbed, dissociated oxygen on copper surfaces behaves as a strong base. $Cu^I(BTA)$ is known to be oxygen sensitive and upon exposure to the atmosphere, it rapidly assumes the characteristic green color of divalent, octahedral copper(II) compounds; X-ray photoelectron spectroscopy measurements in our laboratories have confirmed this oxidation of Cu(I) to Cu(II). We believe, therefore, that air oxidation of the initially-formed Cu(I) benzotriazole leads to a surface phase of Cu(II) benzotriazole.

Monodentate behavior for benzotriazole prevails for four coordinate metals. These include Ir(I) [21] and (in this paper) Zn(II), Cd(II), Hg(II), Pd(II) and Si(IV). Complexes containing monodentate benzotriazole are also formed from excess ligand and hard metal ions capable of expanding their coordination core, as illustrated by Sn(IV) and Ti(IV). Soft metals (or metal ions) which can adopt a higher coordination number tend to generate aggregated or polymeric networks containing η_3 benzotriazole, of which the Tl(I) salt is illustrative [22]. Copper(II) is a conspicuous example of this. The Cu(II) benzotriazole compounds reported here are almost certainly polymeric as evidenced by their characteristic optical spectra, insolubility in non-reactive solvents and by electron spin resonance spectra indicative of ligand-mediated exchange coupling. Polymerization in these materials can occur when all three nitrogen atoms in the benzotriazole ligand are bonded to multiple copper(II) centers. This mode of bonding has recently been established crystallographically in the copper—nitrogen cluster $Cu_5(BTA)_6(t\text{-}C_4H_9\text{-}NC)_5$ [19] and would serve to generate a highly crosslinked polymer.

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