Table II. Isotopic Composition (%) of N_2O As Calculated for Assumed Reaction Source Mixtures and Compared with Observed Values

	12.7 M HNO_3, 12.8% ^{15}N		5.9 M HNO_3, 6.9% ^{15}N	
mass	calcd[a]	obsd	calcd[b]	obsd
46	0.38	0.33	0.40	0.33
45	14.0	14.0	9.62	9.63
44	85.6	85.6	90.0	90.0
44-46[c]	7.37	7.36	5.21	5.15
30 + 31[c]	12.8	12.5	6.91	7.20

[a] Assuming 90 mol % arises from $H_2N{*}NO_2$. [b] Assuming 57 mol % arises from $H_2N{*}NO_2$. [c] % ^{15}N.

metric, bound precursor $H_2N{*}NO_2$ and the other from an unbound intermediate whose nitrogen comes from HNO_3. The latter prescription is met by HNO:

$$H{*}NO + H{*}NO \rightarrow {*}N{*}NO \qquad (3)$$

Reaction 3 would account for the presence of $^{15}N^{15}N^{16}O$ and would also result in production of $^{15}N^{14}N^{16}O$ as well as $^{14}N^{15}N^{16}O$, which in turn can account for the elevation of the overall ^{15}N content of the N_2O. To test this idea we have calculated the detailed isotopic composition of N_2O expected from reactions 2 and 3 separately, at the two different levels of ^{15}N enrichment in HNO_3, by taking into account all possible isomers at masses 44–46 and without neglecting natural abundances of ^{15}N and ^{18}O. As shown in Table II, a very close match between observed and calculated isotopic compositions is obtained when we assume a product containing 90 mol % from (2) and 10 mol % from (3) at $[HNO_3] = 12.7$ M and 57 mol % from (2) plus 43 mol % from (3) at $[HNO_3] = 5.9$ M. The closeness of comparison extends to the electron-impact-produced NO composition (mass 30–31) as well as the individual masses 44–46 and overall N_2O composition.

We conclude that the predominant immediate precursor to N_2O product of the nitric acid–sulfamic acid reaction is indeed nitramide, as proposed by Hughes et al.[8] but that, at least under the slow reaction conditions of our experiments, substantial proportions also arise from the dimerization of an unbound intermediate whose nitrogen atoms come from HNO_3 and which we presume to be HNO. Since N_2O is not a reported or expected product of self-decomposition in HNO_3, we presume that the HNO must have its origins within the HNO_3–NH_2SO_3H reaction itself, a conclusion that is reinforced by the apparent constancy of N_2O isotopic composition with time in the experiment at $[HNO_3] = 12.7$ M (Table I). HNO could be a product of sequential redox processes, but this seems unlikely since unlabeled hydroxylamine and labeled HNO_2 would also be products; interaction of these species would produce N_2O of isotopic composition substantially different from that of either reactions 2 or 3.[10] (Hughes et al.[8] have also considered the possibility of N_2O production by an NH_2OH–HNO_2 reaction; our results appear to rule this out definitively.) We believe it most likely that HNO is produced via decomposition of or a competing reaction with an intermediate which precedes the formation of nitramide. In Scheme 2 of Hughes et al.,[8] for example, it is postulated that the species $ONNHOSO_3H$ is formed and subsequently reacts with HNO_3 on the route to H_2NNO_2. HNO containing nitrogen of the same isotopic content as initial HNO_3 could be formed from this species by N–N cleavage by hydrolysis or some other means. The higher proportion of N_2O from HNO dimerization observed at the lower HNO_3 concentration could then be interpreted in terms of a weaker competition of HNO_3 for reaction with the intermediate.

Separated N_2 produced at $[HNO_3] = 12.7$ M was found to contain 7.3 ± 0.9% ^{15}N, i.e., just half of the initial $H^{15}NO_3$ abundance within error. This product probably arises from reaction between HNO_2 and NH_2SO_3H, which is consistent with the isotopic result. The source of HNO_2 can be self-decomposition of HNO_3 to NO_2 followed by disproportionative hydrolysis and also the nitric acid–sulfamic acid reaction itself, if Scheme 2 of Hughes et al.[8] should be correct. An additional reaction source possibility, which would have the same isotopic consequence, is interaction between HNO_2 and H_2NNO_2.[11]

Acknowledgment. We thank Dr. Charles Iden and the Stony Brook mass spectrometry facility for assistance with isotopic analyses.

Registry No. HNO_3, 7697-37-2; NH_2SO_3H, 5329-14-6; N_2O, 10024-97-2.

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(1) Research supported by the National Science Foundation, Grant No. CHE 76-08766.
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Contribution from Bell Laboratories,
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Preparation and Characterization of Tetrakis(2,4-pentanedionato)hexakis(benzotriazolato)pentacopper(II)

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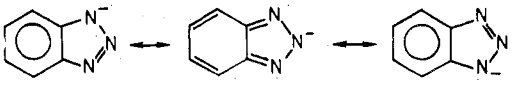
We wish to report some experimental results with the title compound (I) which strongly suggest unique tridentate bonding for each of the benzotriazole anions (BTA^-)



One structure for I consistent with our results is a tetrahedral array of Cu(II) ions surrounding a central Cu(II) ion held together by bridging tridentate BTA^- and terminated by 2,4-pentanedionato ($acac^-$) end caps (Figure 1).[1] It is easily built from molecular models and may be viewed as a $Cu_5BTA_6{}^{4+}$ cation neutralized by four $acac^-$ anions.

Compound I is prepared by mixing equimolar amounts of 0.1 M methanol solutions of $Cu(NO_3)_2{\cdot}3H_2O$, 2,4-pentanedione, and BTA followed by addition of ammonia to basic pH or by mixing dichloromethane solutions of $Cu(acac)_2$ and BTA in equimolar proportions.[2] If the former method is employed, the clear dark green solution is extracted with cyclohexane and the cyclohexane extracts are washed with H_2O and then dried with anhydrous Na_2SO_4. The cyclohexane is removed by evaporation, the green solid is recrystallized from 1,2-dichloroethane–acetonitrile (ca. 1:20), and the deep green crystals are heated overnight in vacuo at 80 °C. Anal. Calcd for $C_{56}H_{52}N_{18}O_8Cu_5$: C, 47.26; H, 3.69; N, 17.73; Cu, 22.33. Found: C, 47.22; H, 3.69; N, 17.65; Cu, 23.12.[3] Osmometric molecular weight determinations yielded 993 ($CHCl_3$)[4] and 1335 (benzene); 1423 is calculated for I.[5] Yields of I based

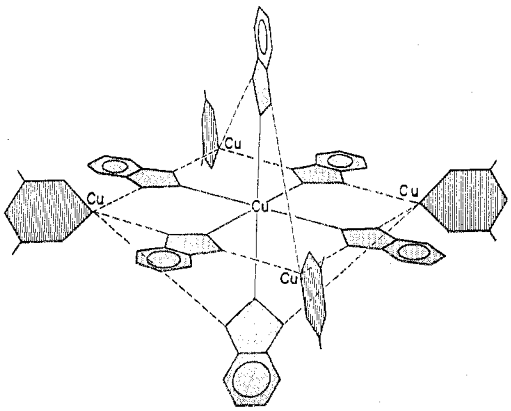


Figure 1. Approximate configuration of $Cu_5(BTA)_6(acac)_4$.[1]

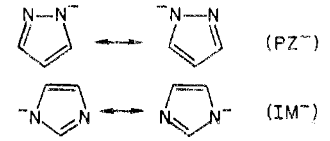
on Cu are typically 60%. Compound I decomposes at 240 °C without melting, and in vacuo no sublimation occurs prior to decomposition. Rhombohedral crystals (with modified trigonal coigns[6]) grown by slow cooling of cyclohexane solutions[7] contained three solvent molecules per molecule of I as indicated by C, H, and N analyses. The IR spectrum of I (747 (s), 770 (m), 793 (m), 930 (w), 1000 (w), 1030 (w), 1190 (m), 1210 (m), 1270 (m), 1390 (s), 1430 (m), 1520 (s), 1590 (s), and 3060 (w) cm^{-1}) dissolved in $CHCl_3$ or CS_2 is dominated by bands attributable to the $acac^-$ ligand. However, the 747-, 1000-, 1190-, and 1210-cm^{-1} bands may be assigned to BTA^- [8-10] and no NH bands are detected. The visible spectrum of I dissolved in $CHCl_3$ or CS_2 consists of a single broad band at ca. 15 000 cm^{-1} characterized by a long tail-off into the near-IR region. Cyclohexane or dichloromethane solutions of I give peaks in the UV at 33 300, 36 400, and 45 500 cm^{-1}.

The room-temperature ESR spectrum[11] of I dissolved in benzene is a symmetrical Lorentzian resonance at $g = 2.1375 \pm 0.0005$ with a peak-to-peak line width of 205 ± 5 G. At −180 °C the g value is 2.1247 ± 0.0005 and the line width is 180 ± 5 G. A single line at $g \simeq 4.3$, much less intense than the $g \simeq 2.13$ resonance, becomes increasingly apparent at maximum microwave power as the temperature is decreased. Its line width is ca. 250 G. The ESR spectrum of a powdered sample of I is nearly indistinguishable from that of a dilute benzene solution. Assuming the presence of five Cu(II) ions per molecular weight of 1423, comparison of benzene solutions of I and bis(3-phenyl-2,4-pentanedionato)copper(II), by double integration of their derivative ESR spectra gives a double integral of I which is 20 ± 5% smaller than that for the monomeric complex. Double integration of the derivative ESR spectrum of I reveals a simple $1/T$ dependence of the magnetic polarization between 20 and −180 °C and rules out substantial antiferromagnetic coupling between the Cu(II) ions.

The simple $1/T$ dependence of the magnetic polarization and the ready displacement of the ligands from $Cu(acac)_2$ by BTA indicate that BTA^- nitrogen atoms rather than $acac^-$ oxygen atoms are bridging the Cu(II) ions of I. If the adjacent nitrogen atoms are involved, the Cu(II)–Cu(II) nearest-neighbor distance is probably 3.5–4.0 Å.[8,12] At this separation both the dipole–dipole and the electron-exchange interactions can be expected to be substantially larger than the isotropic hyperfine interaction ($a_{Cu(II)}$ in many complexes is typically 50 G).[13] Such a situation would explain the broad structureless $g \simeq 2$ ESR resonance. The temperature independence of the $g \simeq 2$ solution ESR spectra and the similarity of solution and polycrystalline ESR spectra suggest significant line width contributions arising from slow molecular tumbling. The weak $g \simeq 4$ resonance confirms the presence of spin-coupled pairs.

Few studies of metal ion complexes containing BTA^- envisage a bonding configuration for BTA^-. One report cites molecular weight evidence for a trimeric or tetrameric cluster of dimethylgallium(III)–BTA^-.[14] The recent description of a complex comprising a linear array of three Ni(II) ions in which each pair of ions is bridged by two BTA^- units includes what is apparently the sole crystal structure determination of a compound containing BTA^-.[8,12] The BTA^- anions are bidentate and the bridge is formed by the adjacent nitrogen atoms. A few reports describe the use of BTA^- as an analytical precipitating agent for various metallic ions[9,15-20] but merely establish the empirical formulas and the low solubility of the polymer-like precipitates obtained. Recent interest has centered on the high corrosion resistance imparted to metal surfaces by BTA^--containing films,[10,21-32] but again no specific information with regard to the disposition of the BTA^- moieties has been reported.

Crystallographic studies of metal ion complexes containing BTA^--related anions, for example derivatives of the anions of pyrazole (PZ^-) or imidazole (IM^-)



frequently reveal both ligands forming bidentate bridges between metal ions.[33-39] The major features of at least two previously reported crystalline structures are comparable to those proposed for I. A ring of four Co(II) ions held together by four IM^- bridges is present in crystals of $Co^{II}(IM)_2$,[38] and crystals of $[Cu_2(bpim)(IM)]_2(NO_3)_4 \cdot 4H_2O$ (bpim = 4,5-bis[2-(2-pyridyl)ethyliminomethyl]imidazolate) contain a similar ring of four Cu(II) ions.[40]

Acknowledgment. The helpful advice of S. H. Glarum and M. L. Kaplan is appreciated.

Registry No. I, 67921-63-5.

References and Notes

(1) The five Cu(II) ions proposed as being in a tetrahedral configuration are illustrated in a single plane. All six BTA^- anions are chemically equivalent in the proposed structure.

(2) Both preparative methods require a [Cu(II)]/[BTA] ratio of 1.0 for high yields of I. Ratios greater than 1.0 will lead to light green crystals soluble in cyclohexane but different in morphology from I. Ratios less than 1.0 will cause precipitation of light green solids, presumably largely $Cu^{II}(BTA)_2$.

(3) A Perkin-Elmer 240 elemental analyzer was used to determine C, H, and N. Cu was determined utilizing atomic absorption spectroscopy by L. D. Blitzer of this laboratory.

(4) The low molecular weight obtained for I in $CHCl_3$ corresponds to ca. half the molecules of I being ionized in this solvent according to I $\rightleftarrows$ $[Cu_5(BTA)_6(acac)_3]^+ + acac^-$. The recrystallization procedure employed for I coupled with the nearly theoretical C, H, and N analyses discounts the possibility that I dissociates into smaller fragments such as $Cu_2(BTA)_2(acac)_2$ or $Cu_3(BTA)_4(acac)_2$.

(5) Molecular weight determinations were performed by Gailbraith Laboratories, Inc., Knoxville, Tenn., and by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

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(7) The solubility of I in cyclohexane is greater than 0.1 M.

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Characterization of the Coordination Properties of Bis(3,5-dimethylpyrazole-1-carbodithioato)copper(II)

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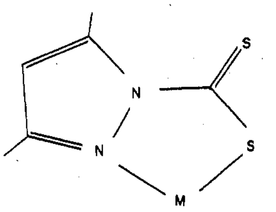
The coordination chemistry of sulfur-containing ligands has attracted a great deal of attention in recent years.[1-4] Our work in this area has centered on the preparation and characterization of the electronic properties of new dithiolate and dithiocarbamate ligands. We have been particularly interested in the design of ligands which promise to induce unusual electronic properties at metal centers. For example, we recently reported the preparation of new dithiocarbamate ligands derived from pyrrole,[5] indoline, indole, carbazole, and imidazole,[6] exploiting a route first outlined by Trofimenko[7] in the preparation of pyrazolecarbodithioates. Our characterization of these ligands and selected transition-metal complexes indicated that each complex contained quite stable MS$_4$ chromophores, and furthermore, each behaved as a strong-field ligand. Interestingly, Trofimenko suggested that the coordination properties of the ambidentate pyrazolecarbodithioate ligands produced instead N$_2$S$_2$ coordination environments. The argument for this chromophore was based mainly on the extra stability associated with a five-membered chelate ring (including the metal) (I) compared to a four-membered ring (II).



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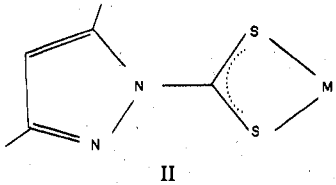

II

Table I. Spin-Hamiltonian Parameters for Bis(3,5-dimethylpyrazole-1-carbodithioato)copper(II)

solvent	A_0, G	g_0	$A_{\parallel}$, G	$g_{\parallel}$	$A_{\perp}$,[b] G	$g_{\perp}$[a]	$g_{\perp}$[b]	$A_{\parallel}^{N}$
CHCl$_3$-DMF	67.7	2.064	171	2.164	16.1	2.014	2.067	16.1
CHCl$_3$-Me$_2$SO	67.1	2.064	173	2.163	15.2	2.015	2.067	16.3

[a] Calculated from approximations for axially symmetric complexes: $A_0 = (A_{\parallel} + 2A_{\perp})/3$; $g_0 = (g_{\parallel} + 2g_{\perp})/3$. [b] Observed.

In previous cases of ambidentate ligands, where an MS$_4$ or MN$_2$S$_2$ coordination environment was possible, the MS$_4$ chromophore resulted.[8] Since Trofimenko presented no data to substantiate an N$_2$S$_2$ coordination for the title ligand, we felt it necessary to more carefully investigate this system since it led us to develop a new class of compounds.

Experimental Section

Materials. Tetrahydrofuran (THF) and hexanes were dried by standard procedures and distilled immediately before use. Carbon disulfide was dried over Davison 4 Å molecular sieves. Anhydrous copper(II) bromide was obtained from Research Organic/Inorganic Inc. and used without purification, and 3,5-dimethylpyrazole was prepared by a literature method.[9]

Synthesis. Preparation of Potassium 3,5-Dimethylpyrazole-1-carbodithioate. Synthesis of this compound was accomplished by the method of Trofimenko[7] except that THF was used as the solvent, and the reaction was carried out under an argon atmosphere.

Preparation of Bis(3,5-dimethylpyrazole-1-carbodithioato)copper(II). To 150 mL of THF were added 2.00 g (9.6 mmol) of the potassium salt of the ligand and 0.992 g (4.4 mmol) of CuBr$_2$ under an argon atmosphere. The resulting red-brown solution was stirred at room temperature for 5 h and filtered to remove KBr. The filtrate was rotary evaporated to a volume of ~75 mL, and hexanes were then added to the point of incipient precipitation. Chilling of this solution at −20 °C for 24 h resulted in the formation of 1.315 g of dark red-brown crystals. Due to the instability of the compound, we were not able to obtain an elemental analysis.

Magnetic Susceptibility Determination. Susceptibilities were determined on solid samples at 27 °C using the Gouy method. Pascal's constants were used to correct the measurements for diamagnetic contributions of the ligands and core electrons of the metal.[10]

Spectroscopic Measurements. Infrared spectra were obtained as KBr pellets on a Perkin-Elmer 467 spectrometer. ESR spectra were determined at ~9.0 GHZ employing a Varian E-9 spectrometer coupled to a Hewlett-Packard frequency meter and DPPH as a g-value standard. Visible spectra were obtained in solution in DMF and as a mull in Nujol with a Cary 14 spectrophotometer.

Results and Discussion

The Cu(II) compound of 3,5-dimethylpyrazole-1-carbodithioate is unstable both in the solid state and in solution. It is readily soluble in polar organic solvents such as DMF, Me$_2$SO, and CH$_3$CN. The positions of the optical peaks of this compound are identical in the solid state and in solution and are characteristic of a four-coordinate square-planar Cu(II) complex. The infrared spectrum shows identifying absorptions at 1575 cm^{-1} (pyrazole ring), 1340 cm^{-1} (C=S), and 390 cm^{-1} (Cu—S). No absorptions from solvent molecules appear present, precluding a solvated complex.

The copper(II) compound was the metal system chosen to characterize since, in principle, a great deal of information about the nature of the coordination environment can be obtained by the determination of the spin-Hamiltonian parameters from the electron spin resonance (ESR) spectra. These parameters for the copper(II) complex obtained in various solvents are listed in Table I. Much to our surprise, five well-resolved ligand hyperfine lines ($A_{\parallel}^{N}$ = 16.1 G) due to two equivalent nitrogen atoms were evident in the glass and solution spectra (see Figure 1). This observation alone characterizes the chromophore as a CuN$_2$S$_2$ one. In addition, the values of the principal g value and metal hyperfine coupling

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