make the bismuth six-coordinate. There is a possibility that one of the hydroxide groups is displaced, at least in part, by the γ gluconate oxygen in the 1:1 complex; this appears to be true especially at high pH values. At pH values above pH 14 the carboxylate groups in the 1:1 complex appear to be displaced by hydroxide ions; this apparently does not occur to a significant extent for the 1:1 complex (Figure 6).

In general the interactions between the gluconate ion and lead and bismuth ions appear quite similar to those observed for the tartrate ion.[5] Under alkaline conditions bonding to the alcoholic oxygens is accomplished by displacement of the proton. Of the soluble diamagnetic ions studied only lead and bismuth exhibit coordination by the alcoholic oxygens. However, a number of paramagnetic ions are known to be complexed strongly by gluconate ion,[1] especially iron(III), copper(II), and the rare earths. Unfortunately proton n.m.r. studies are not possible because of the strong relaxation effects upon the line widths. However, the donor groups involved in bonding to the paramagnetic ions can reasonably be concluded to be the same as those observed for the lead and bismuth ions under similar solution conditions. Thus, a general conclusion is that the α, β, and γ oxygen atoms of the gluconate ion together with the carboxylate group are the effective donor groups for complexation under alkaline conditions.

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Broad-Line Proton Magnetic Resonance Spectra of Dichloro(1,2,4-triazole)copper(II) and Bis(1,2,4-triazolato)copper(II)

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The broad-line p.m.r. spectrum of dichloro(1,2,4-triazole)copper(II) consists of two absorptions of intensity ratio equal to 2:1, indicating the existence of two kinds of nonequivalent hydrogen atoms in crystals in agreement with the results of X-ray analysis. The spectrum of bis(1,2,4-triazolato)copper(II) comprises two absorptions of equal intensity, indicating the existence of two kinds of nonequivalent hydrogen atoms in crystals. From the observed field shifts due to Fermi contact hyperfine interaction, the spin densities on atoms in the nitrogen heterocycles were evaluated. On the basis of this information, along with magnetic data obtained earlier, possible structures are proposed for this compound.

Introduction

In a preceding paper,[1] we have reported the results of measurements on the magnetic moments of a variety of copper(II) complexes having nitrogen heterocycles as ligands. It was found that whereas a normal magnetic moment of 1.81 B.M. was observed for dichloro(1,2,4-triazole)copper, bis(1,2,4-triazolato)copper(II) shows a subnormal magnetic moment, 1.66 B.M., at room temperature, suggesting the existence of copper atoms magnetically coupled in pairs. In order to obtain further information on the structure of these complexes, we have recorded the broad-line p.m.r. spectra and evaluated the spin densities on atoms in the nitrogen heterocycles from the observed field shifts due to Fermi contact hyperfine interaction.

Experimental Section

The powdered crystals of dichloro(1,2,4-triazole)copper(II) and bis(1,2,4-triazolato)copper(II) were prepared as described in a previous report.[1]

The p.m.r. spectra of these compounds were recorded at 24° by means of a Model JNS-B broad-line n.m.r. spectrometer from Japan Electron Optics Laboratory Co. operating at 35.45 Mc. with an amplitude of magnetic field modulation of 1.0 oersted. Since high-resolution chemical shifts are trivial in broad-line n.m.r. spectra, any diamagnetic hydrogen-containing compounds may be used as a reference. We employed water as an external standard. A small amount of copper(II) sulfate was dissolved in it in order to facilitate spin relaxation.

Results

The observed absorption derivative curves are shown in Figure 1. The curve of dichloro(1,2,4-triazole)-copper(II) is asymmetric and can be decomposed into two simple derivative curves of intensity ratio equal to 2:1 as shown in Figure 1a. The curve observed for bis(1,2,4-triazolato)copper(II) also is composite and is made up of two simple curves of equal intensity superposed on each other. The observed nuclear resonance field shifts $\Delta H/H$ are shown in Table I.

Discussion

The X-ray crystal analysis of dichloro(1,2,4-triazole)-copper(II) has been carried out by Jarvis,[2] who found that all 1,2,4-triazole molecules are equivalent in the crystal and that two neighboring nitrogen atoms in a molecule of the nitrogen heterocycle are coordinated

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(1) M. Inoue, M Kishita, and M. Kubo, *Inorg. Chem.*, **4**, 626 (1965).

(2) J. A. J. Jarvis, *Acta Cryst.*, **15**, 964 (1962).

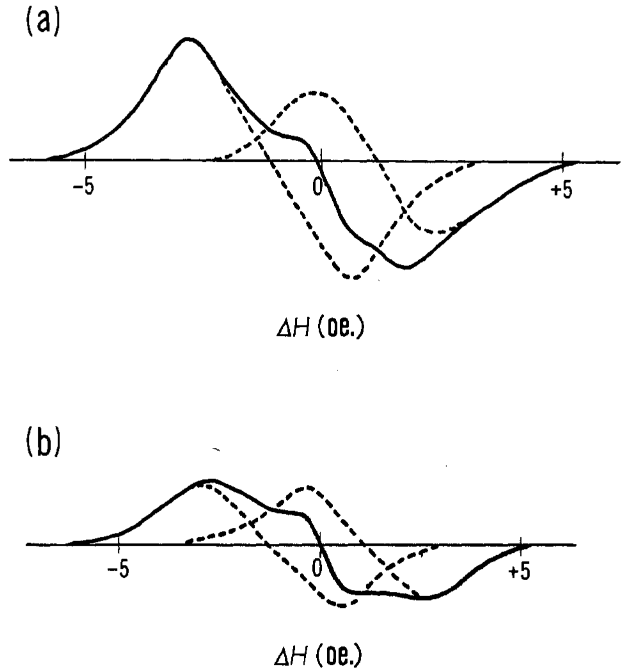

Figure 1.—P.m.r. absorption derivative curves of (a) dichloro(1,2,4-triazole)copper(II) and (b) bis(1,2,4-triazolato)copper(II). Each observed curve (full curve) is the superposition of two simple derivative curves (broken curves).

TABLE I
THE EFFECTIVE MAGNETIC MOMENTS, CONTACT INTERACTION SHIFTS, CONTACT INTERACTION CONSTANTS, AND SPIN DENSITIES OF DICHLORO(1,2,4-TRIAZOLE)COPPER(II) AND BIS(1,2,4-TRIAZOLATO)COPPER(II)

Compound	μ, B.M.	$\Delta H/H$ $\times 10^4$	Relative intensity	a_i, oersteds	ρ_i
$CuCl_2(TrH)$[a]	1.81	-1.3	2 (CH)	$+1.6$	-0.07
		$+1.4$	1 (NH)	-1.7	$+0.05$
$Cu(Tr)_2$	1.66	-1.7	1 (CH)	$+2.5$	-0.10
		$+1.3$	1 (CH)	-1.9	$+0.08$

[a] TrH, 1,2,4-triazole.

on two copper atoms bridged by two chlorine atoms, copper atoms being arranged in a one-dimensional array as shown in Figure 2. From the intensity ratio, 2:1, of the two absorptions showing different contact interaction shifts, the stronger one on the low-field side is assigned unequivocally to protons bonded to carbon while the high-field absorption is attributable to those bonded to nitrogen.

The isotropic contact hyperfine interaction field ΔH is given by[3-7]

$$\frac{\Delta H}{H} = -a_i\left(\frac{\gamma_e}{\gamma_N}\right)\frac{g\beta S(S+1)}{3kT} \tag{1}$$

where H is the nuclear resonance field; a_i is the contact interaction constant; γ_e and γ_N are the magnetogyric ratios of an electron and a nucleus, respectively; $g = 2.00$ is the electronic g factor; β denotes the Bohr mag-

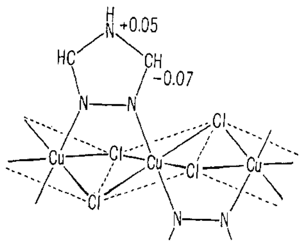

Figure 2.—Spin density distribution in a 1,2,4-triazole molecule of dichloro(1,2,4-triazole)copper(II).

neton; S is the electron spin quantum number; and k and T denote the Boltzmann constant and the absolute temperature, respectively. Since the effective magnetic moment μ is given by $\mu = g\beta[S(S+1)]^{1/2}$, one has

$$\frac{\Delta H}{H} = -a_i\left(\frac{\gamma_e}{\gamma_N}\right)\frac{\mu^2}{3g\beta kT} \tag{2}$$

Therefore, from the observed nuclear resonance field shift $\Delta H/H$ and the effective magnetic moment μ, the contact interaction constant a_i can be calculated as shown in Table I.

The foregoing theoretical derivation is based on Fermi contact interaction and disregards the pseudo-contact interaction arising from the combined effects of electron spin–nuclear spin coupling, electron orbit–nuclear spin coupling, and electron spin–electron orbit interaction. In order to justify this, the isotropic field shift due to pseudo-contact interaction in polycrystalline solids was estimated[5] by use of X-ray data on dichloro(1,2,4-triazole)copper(II) and assumed g values, $g_{||}$ and $g_{\perp}$. The field shift $\Delta H/H$ is at most 0.04×10^{-4}, which amounts to only a few per cent of the observed shifts.

McConnell[4,6,8] has shown that for aromatic radical species, in which a spin density localized on a pπ orbital of a carbon atom interacts with a proton bonded to the carbon atom, the contact interaction constant a_i of a proton is related to the spin density ρ_i on the adjacent carbon atom by

$$a_i = Q\rho_i \tag{3}$$

where Q is a proportionality constant characteristic of the particular mechanism giving rise to the **IS** interaction between a nuclear spin I and an electron spin S.

The absolute values for Q have been determined by electron spin resonance experiments on a variety of free radicals. The sign of Q is not determinable from the e.s.r. experiments. However, the signs of ρ in paramagnetic systems are manifested in n.m.r. experiments by the direction of resonance field shifts. Thus, Q for aromatic ·C–H fragments has been empirically determined as $Q(\mathrm{CH}) = -22.5$ oersteds as an average value.[4,6,9]

On the other hand, few data are available in the literature on the values of Q(NH) for protons bonded to a nitrogen atom involved in a heterocyclic ring. Barton

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[4] H. M. McConnell and D. B. Chesnut, *ibid.*, **28**, 107 (1958).
[5] H. M. McConnell and R. E. Robertson, *ibid.*, **29**, 1361 (1958).
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[7] E. L. Muetterties and W. D. Phillips, *Advan. Inorg. Chem. Radiochem.*, **4**, 231 (1962).
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[9] T. R. Tuttle and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 5342 (1958).

and Fraenkel[10] have carried out electron spin resonance experiments on pyrazine cation radicals. By use of $Q(\mathrm{CH}) = -23.7$ oersteds, they obtained $Q(\mathrm{NH}) = -33.7$ oersteds for protons attached to nitrogen. Since the sign and the approximate values of spin densities are crucial while accurate values thereof are rather immaterial in the present discussion, we have assumed that $Q(\mathrm{CH}) = -24$ oersteds and $Q(\mathrm{NH}) = -34$ oersteds and calculated the spin densities ρ_i from the observed contact interaction constants a_i as shown in Table I.

The spin densities calculated for dichloro(1,2,4-triazole)copper(II) are reasonable both in their signs and the order of magnitude as compared with those of metalocenes[11] and some N,N′-substituted aminotropoloneiminenickel(II) derivatives.[12,13]

The crystal structure of bis(1,2,4-triazolato)copper(II) has not been investigated by X-ray crystal analysis as yet. Contrary to a simple expectation, we have found two absorptions showing contact interaction shifts of different signs. This indicates that two kinds of nonequivalent hydrogen atoms exist in crystals. There are two possibilities. First, it is conceivable that two hydrogen atoms attached to ring positions 3 and 5 in a 1,2,4-triazolato group are nonequivalent owing to an asymmetric way in which the ligand is coordinated on copper atoms. Alternatively, one may presume that although two hydrogen atoms in a 1,2,4-triazolato group are equivalent to each other, two kinds of nonequivalent ligand groups exist in equal abundance. From this choice along with conclusions capable of being derived from the observed magnetic moment and spin densities, one can draw a fairly concrete picture for the crystal structure satisfying these requirements.

A considerable number of copper(II) complexes are known to show subnormal magnetic moments.[14] However, the type of coupling scheme of unpaired electron spins belonging to copper atoms is rather limited. In copper(II) acetate monohydrate,[15] copper atoms are bridged in pairs by four –O–C–O– groups of *syn-syn* arrangement. A majority of copper(II) carboxylates are believed to have the same type of paired copper atoms.[16–18] In the so-called tricoordinated copper(II) complexes,[19–21] copper atoms are bridged in pairs by two oxygen atoms, as was confirmed by X-ray crystal analysis carried out by Barclay, *et al.*,[22] on acetylacetonemono(*o*-hydroxyanil)copper(II). The copper(II) chloride complex with pyridine N-oxide has been shown by a complete X-ray crystal structure examination[23,24] to have the same binuclear oxygen-bridged structure. Lastly, in copper(II) formate tetrahydrate,[25] copper atoms are linked by –O–C–O– groups of *anti-anti* arrangement to form a layer structure. It is known theoretically as well as experimentally that copper(II) complexes having one-dimensional arrays of equally spaced copper atoms do not show subnormal magnetic moments, because long-range spin interaction is absent in such structures.[1,26]

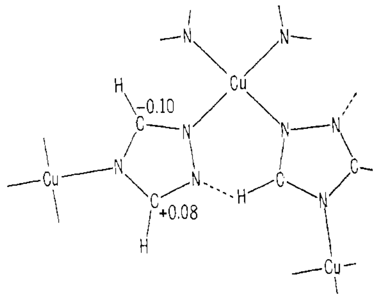

Figure 3.—Spin density distribution in a suggested structure of bis(1,2,4-triazolato)copper(II).

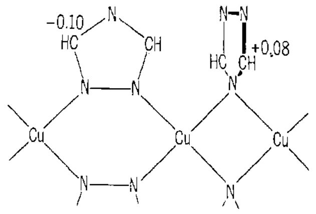

Figure 4.—Spin density distribution in an alternative structure of bis(1,2,4-triazolato)copper(II).

For steric reasons, the *syn-syn* bridging arrangement as in copper(II) acetate monohydrate is impossible for a 1,2,4-triazolato group. If it is assumed that the group is coordinated unsymmetrically on copper atoms through nitrogens at positions 2 and 4 so that two hydrogen atoms attached to carbon atoms 3 and 5 are nonequivalent, a structure is conceivable in which copper atoms are bridged by *anti-anti* –N–C–N arrangements to form a two-dimensional structure as in copper(II) formate tetrahydrate. A possible structure is shown in Figure 3. On the other hand, if it is assumed that two kinds of nonequivalent ligand groups each having equivalent hydrogen atoms exist in crystals, an alternative structure shown in Figure 4 suggests itself as a plausible possibility, in which copper atoms are bridged in pairs by two nitrogen atoms rather than by two oxygen atoms as in acetylacetonemono(*o*-hydroxyanil)copper(II).

These two proposed structures are checked below by

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comparison of the observed spin densities with those estimated from valence bond calculations.

A cyclopentadienyl group, $C_5H_5^-$, which is isoelectronic with a 1,2,4-triazolato group, represents a five-membered ring system accommodating five π electrons. The molecular orbital calculation leads to a conclusion that the unpaired electron is uniformly distributed among five carbon atoms. The same conclusion is reached by the valence bond method if five resonance structures having an unpaired electron at different carbon atoms contribute equally to the normal state. In a 1,2,4-triazolato group coordinated on a copper atom through nitrogen at position 4, the uniformity of charge distribution must be destroyed in such a way that the spin density at this nitrogen atom is closer to unity. However, it is hardly believable that spin densities are altered in their signs. In other words, positive spin densities are expected for all ring members.

For a 1,2,4-triazolato group coordinated on two copper atoms through nitrogen atoms 1 and 2, the electronic structure is represented, to a first approximation, by a resonance hybrid between two resonance structures, I and II, having an unpaired electron at positions 1 and 2, respectively. The corresponding wave functions, apart from the normalizing factor, are given by

$$\phi_{\text{I}} = \alpha\alpha\beta\alpha\beta - \alpha\alpha\beta\beta\alpha - \alpha\beta\alpha\alpha\beta + \alpha\beta\alpha\beta\alpha \tag{4a}$$

$$\phi_{\text{II}} = \alpha\alpha\beta\alpha\beta - \alpha\alpha\alpha\beta\beta - \beta\alpha\beta\alpha\alpha + \beta\alpha\alpha\beta\alpha \tag{4b}$$

where spin functions, α and β, are arranged in the order of conventional numbering of ring members in organic chemistry. The wave function representing the resonance hybride is

$$\psi = \phi_{\text{I}} + \phi_{\text{II}} \tag{5}$$

The π electron spin density ρ_n on the nth ring atom is given by[4,27]

$$\rho_n = \langle\psi|\varrho_n|\psi\rangle = \langle\phi_{\text{I}}|\varrho_n|\phi_{\text{I}}\rangle + \langle\phi_{\text{II}}|\varrho_n|\phi_{\text{II}}\rangle + 2\langle\phi_{\text{I}}|\varrho_n|\phi_{\text{II}}\rangle \tag{6}$$

The spin density operator ϱ_n operates on the nth factor of each term in the right-hand side of eq. 4 with an eigenvalue $\pm{}^1/_2$ depending on whether the nth factor is α or β. Accordingly, one has

$$\langle\phi_{\text{I}}|\varrho_1|\phi_{\text{I}}\rangle = \frac{1}{2}\langle\alpha\alpha\beta\alpha\beta|\alpha\alpha\beta\alpha\beta\rangle + \frac{1}{2}\langle\alpha\alpha\beta\beta\alpha|\alpha\alpha\beta\beta\alpha\rangle + \frac{1}{2}\langle\alpha\beta\alpha\alpha\beta|\alpha\beta\alpha\alpha\beta\rangle + \frac{1}{2}\langle\alpha\beta\alpha\beta\alpha|\alpha\beta\alpha\beta\alpha\rangle \tag{7}$$

All other terms vanish because of the orthogonality of spin wave functions, α and β. Therefore

$$\langle\phi_{\text{I}}|\varrho_1|\phi_{\text{I}}\rangle = {}^1/_2 + {}^1/_2 + {}^1/_2 + {}^1/_2 = 2 \tag{8a}$$

Similar calculations lead to

$$\langle\phi_{\text{I}}|\varrho_2|\phi_{\text{I}}\rangle = {}^1/_2 + {}^1/_2 - {}^1/_2 - {}^1/_2 = 0 \tag{8b}$$

and so forth. Thus, one has

$$\begin{aligned}\langle\phi_{\text{I}}|\varrho_n|\phi_{\text{I}}\rangle &= 2 \quad (n = 1)\\ &= 0 \quad (n \neq 1)\end{aligned} \tag{9a}$$

and also

$$\begin{aligned}\langle\phi_{\text{II}}|\varrho_n|\phi_{\text{II}}\rangle &= 2 \quad (n = 2)\\ &= 0 \quad (n \neq 2)\end{aligned} \tag{9b}$$

As regards the cross term, one has

$$\langle\phi_{\text{I}}|\varrho_n|\phi_{\text{II}}\rangle = \langle\alpha\alpha\beta\alpha\beta|\varrho_n|\alpha\alpha\beta\alpha\beta\rangle \tag{10}$$

because ϕ_{I} and ϕ_{II} have a single term, $\alpha\alpha\beta\alpha\beta$, in common. Accordingly

$$\begin{aligned}\langle\phi_{\text{I}}|\varrho_n|\phi_{\text{II}}\rangle &= +{}^1/_2 \quad (n = 1,\ 2,\ \text{or}\ 4)\\ &= -{}^1/_2 \quad (n = 3\ \text{or}\ 5)\end{aligned} \tag{11}$$

Introducing eq. 9 and 11 into eq. 6, one has

$$\rho_1 = \rho_2 = 3; \quad \rho_3 = \rho_5 = -1; \quad \rho_4 = 1 \tag{12}$$

Upon normalization to $\Sigma\rho_n = 1$ over ring atoms 1–5, this gives spin densities +0.6 on nitrogen atoms 1 and 2, −0.2 on carbon atoms 3 and 5, and +0.2 on nitrogen atom 4. Thus, the assignment of the observed spin densities as shown in Figure 4 is adequate at least in their signs.

A similar calculation has been made on the same ligand group coordinated on two copper atoms through nitrogen atoms 1 and 4 by taking into account two resonance structures, I and II, having an unpaired electron at positions 1 and 4, respectively. From

$$\phi_{\text{I}} = \alpha\alpha\beta\alpha\beta - \alpha\beta\alpha\alpha\beta - \alpha\alpha\beta\beta\alpha + \alpha\beta\alpha\beta\alpha \tag{13a}$$

$$\phi_{\text{II}} = \alpha\alpha\beta\alpha\beta - \alpha\beta\alpha\alpha\beta - \beta\alpha\beta\alpha\alpha + \beta\beta\alpha\alpha\alpha \tag{13b}$$

one has spin densities

$$\rho_1 = \rho_4 = 4; \quad \rho_2 = \rho_3 = 0; \quad \rho_5 = -2 \tag{14}$$

yielding normalized spin densities $-{}^1/_3$ on carbon atom 5 and $+{}^2/_3$ on nitrogen atoms 1 and 4, whereas nitrogen atom 2 and carbon atom 3 have vanishing spin densities.

The calculation is based on an oversimplification, the greater electronegativity of nitrogen than that of carbon being disregarded. The inclusion of resonance structures having an unpaired electron at positions other than 1 and 4 leads to a qualitative conclusion that the spin density on carbon atom 3 is positive. Accordingly, it is reasonable to assign the observed spin densities to two carbon atoms in a ring as shown in Figure 3. Thus, it is concluded that two observed spin densities differing in sign can be explained adequately by either of the two proposed structures.

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