Structural and Magnetic Properties of Copper(II) Dimers Bridged by Oxalate, Azide, and Cyanide Ions; *X*-Ray Structures of $[Cu_2\{EtN(CH_2CH_2NEt_2)_2\}_2(C_2O_4)][BPh_4]_2$ and $[Cu_2\{MeN(CH_2CH_2NMe_2)_2\}_2(N_3)_2][BPh_4]_2$. The Role of the Transition-metal Ion Ground State in Magnetic Exchange Interactions

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Summary Variable-temperature (4·2—270 K) magnetic susceptibility, e.s.r., and single-crystal *X*-ray crystallographic data are presented to show that a predominantly d_{z^2} Cu^{II} ground state can lead to appreciable magnetic exchange interactions *via* the extended bridges in $[Cu_2(Et_5dien)_2(C_2O_4)][BPh_4]_2$, $[Cu_2(Me_5dien)_2(N_3)_2][BPh_4]_2$, and $[Cu_2(tren)_2(CN)][PF_6]_3$ [$Et_5dien = EtN(CH_2CH_2NEt_2)_2$, $Me_5dien = MeN(CH_2CH_2NMe_2)_2$, and tren = $N(CH_2CH_2NH_2)_3$].

There has been recent interest in magnetic exchange interactions as propagated by extended bridges (> *ca.* 5·0 Å) in dimeric transition-metal complexes.[1] It is becoming clear that it is not simply the distance between the transition-metal ions that determines the magnitude of the exchange interaction across an extended bridging group. We have recently found that appreciable exchange interactions are possible between two Cu^{II} ions *via* μ-oxalato ($C_2O_4^{2-}$), di-μ(1,3)-azido, and μ-(1,2)-cyano bridges with a predominantly d_{z^2} Cu^{II} ion ground state. Our recent structural and magnetic work on three copper(II) dimers reported herein supports this.

The single-crystal *X*-ray structure of $[Cu_2(Et_5dien)_2(C_2O_4)][BPh_4]_2$† was solved using 2679 ($F_{obs} \geqslant 3\sigma$) independent reflections collected on a Picker FACS-1 diffractometer with anisotropic thermal parameters on all non-hydrogen atoms (hydrogen atom positions were computer-generated and assigned isotropic thermal parameters of the

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† $Et_5dien = EtN(CH_2CH_2NEt_2)_2$; $Me_5dien = MeN(CH_2CH_2NMe_2)_2$; tren = $N(CH_2CH_2NH_2)_3$.

atom to which they were attached). As illustrated in Figure 1,‡ the local environments of the copper(II) ion in the oxalate-bridged dimer approximate to trigonal bipyramids. We had selected the ligand Et_5dien to enforce such a geometry because it is known[2] that this ligand would lead to a d_{z2} ground state for Cu^{II} ions. The Q-band e.s.r. spectrum (g_1 2·020, g_2 2·119, and g_3 2·242) of this compound substantiates this with one g-value close to a value of 2·0. The effectiveness of the d_{z2} ground state in propagating a magnetic exchange interaction in this oxalate-bridged dimer is reflected by a maximum in the susceptibility at 60 K, which indicates the presence of an antiferromagnetic exchange interaction with $J = -37$ cm^{-1} (least-squares fitting of the data to the Bleaney-Bowers' equation[3] with $H = -2JS_1 \cdot S_2$). Among the previously studied oxalate-bridged Cu^{II} dimers, $[Cu_2(tren)_2(C_2O_4)][BPh_4]_2$ and $[Cu_2(dien)_2(C_2O_4)][ClO_4]_2$[4] have $|J| <$ *ca.* 0·5 cm^{-1}, while $[Cu_2(dien)_2(C_2O_4)][BPh_4]_2$[5] has $J = -7{\cdot}4$ cm^{-1}. These three compounds have local Cu^{II} environments that lead to other than d_{z2} ground states and, consequently, weaker exchange interactions.

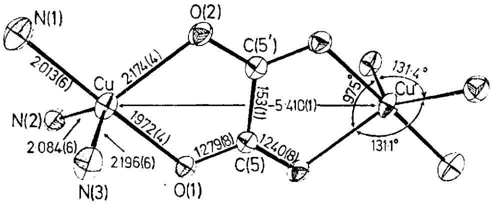

FIGURE 1. View of the inner co-ordination sphere of $[Cu_2(Et_5\text{-}dien)_2(C_2O_4)]^{2+}$ showing only the copper, amine nitrogen, and oxalate-bridge atoms. The dimer is located about an inversion centre.

The single-crystal X-ray structure of $[Cu_2(Me_5dien)_2(N_3)_2][BPh_4]_2$ was solved with anisotropic thermal parameters for all non-hydrogen atoms (hydrogen atoms were given isotropic thermal parameters) using 3140 ($F_{obs} \geqslant 3\sigma$) independent reflections collected on a Syntex $P\bar{1}$ diffractometer. The co-ordination geometry in the di-μ-azido bridged dimer is shown in Figure 2.§ This is the first case of an end-to-end bridging azide ion in a Cu^{II} dimer. End-to-end azide bridging is present in polymeric $Cu(N_3)_2$[6] and in one Cu^I dimer.[7] The local environment at each copper^{II} ion in $[Cu_2(Me_5dien)_2(N_3)_2]^{2+}$ can be viewed as intermediate between a trigonal bipyramid and a square pyramid. The X-band e.s.r. spectrum (6—300 K) of this compound is temperature-dependent and complicated by relatively large zero-field splittings. A maximum at 11 K in the magnetic susceptibility data (fit to $J = -6{\cdot}5$ cm^{-1}) again shows that some degree of the d_{z2} configuration in the Cu^{II} ion ground state can give rise to appreciable antiferromagnetic interaction propagated by an extended bridging group.

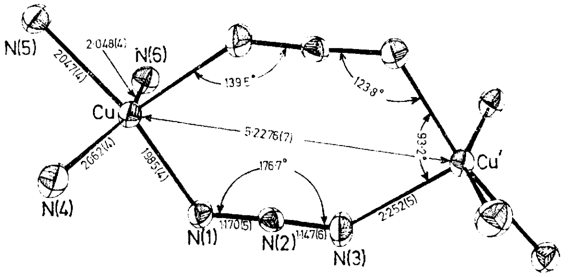

FIGURE 2. View of the inner co-ordination sphere of $[Cu_2(Me_5dien)_2(N_3)_2]^{2+}$ showing only the copper, amine nitrogen, and azide-bridge atoms. The dimer is located about an inversion centre.

Perhaps the most dramatic demonstration of the effectiveness of the Cu^{II} d_{z2} ground state for magnetic exchange comes from our work on $[Cu_2(tren)_2(CN)][PF_6]_3$. It is well known[8] that the tripodal ligand tren enforces a trigonal-bipyramidal geometry on a Cu^{II} ion and that the remaining co-ordination site is axial. End-to-end cyanide ion bridging is known for one Cu^{II} dimer,[9] and with these ideas in mind we have prepared $[Cu_2(tren)_2(CN)][PF_6]_3$, in which a single cyanide ion most probably bridges in an end-to-end fashion between two $Cu(tren)^{2+}$ units. Substantiation for the presence of end-to-end cyanide bridging comes from an antiferromagnetic exchange interaction with J fit to -88 cm^{-1}, the low intensity of the C–N stretch in the i.r. spectrum, and a Q-band e.s.r. spectrum which shows a single, slightly asymmetric derivative. Such an e.s.r. signal can only result from a dimer with end-to-end cyanide bridging where the two Cu^{II} ions are in different environments and the large exchange interaction leads to an exchange-averaged e.s.r. signal. The most important point to make about $[Cu_2(tren)_2(CN)][PF_6]_3$, however, is that the relatively large exchange interaction results from axial bridging with a trigonal-bipyramidal d_{z2} ground state.

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‡ *Crystal data:* monoclinic, space group $P2_1/n$ (non-conventional); $a = 9{\cdot}776(5)$, $b = 25{\cdot}004(12)$, $c = 14{\cdot}551(6)$ Å; $\beta = 91{\cdot}83(2)°$; $M = 1340{\cdot}46$, $Z = 2$ dimers; $D_c = 1{\cdot}26$, $D_m = 1{\cdot}25(2)$ g cm^{-3}; $R_F = 0{\cdot}069$, $R_{WF} = 0{\cdot}056$.

§ *Crystal data:* monoclinic, space group $P2_1/n$ (non-conventional); $a = 12{\cdot}798(2)$, $b = 19{\cdot}538(3)$, $c = 13{\cdot}072(2)$ Å; $\beta = 93{\cdot}64(1)°$; $M = 1196{\cdot}21$, $Z = 2$ dimers; $D_c = 1{\cdot}218$, $D_m = 1{\cdot}215$ g cm^{-3}; $R_F = 0{\cdot}051$, $R_{WF} = 0{\cdot}058$.

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[2] Although there is no work reported on Et_5dien copper complexes, Et_4dien copper complexes are known to be trigonal bipyramidal; see R. F. Ziolo, M. Allen, D. D. Titus, H. B. Gray, and Z. Dori, *Inorg. Chem.*, 1972, **11**, 3044 and references therein.

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