$Cr(CO)_2(CS)[(CH_3O)_3P]_3$ with octahedral *mer* stereochemistry. The CO groups are mutually trans, and the CS ligand is trans to one of the trimethyl phosphite ligands. The explanation for this stereochemical preference does not appear to originate with steric effects since $Cr(CO)_3L_3$ complexes (L = THF, CH_3CN, R_3P), when synthesized under the same conditions as those employed here, are isolated as *fac* isomers even though they are significantly distorted due to steric effects. The formation of only

one of the two possible *mer* isomers of $Cr(CO)_2(CS)[(CH_3O)_3P]_3$ further suggests that the stereochemical preference is dictated by the electronic properties of the thiocarbonyl ligand.

(22) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Further Insight into Magnetostructural Correlations in Binuclear Copper(II) Species Related to Methemocyanin: X-ray Crystal Structure of a 1,2-μ-Nitrito Complex

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The X-ray crystal structure of the nitrite complex $[Cu_2(L-Et)(NO_2)][ClO_4]_2$ (HL-Et = N,N,N',N'-tetrakis(2-(1-ethylbenzimidazolyl))-2-hydroxy-1,3-diaminopropane) has been determined as a further test of the hypothesis of $d_{x^2-y^2}/d_{z^2}$ *orbital switching* which was used to explain the markedly different magnetic properties of the analogous azide and acetate complexes. Crystal data: monoclinic, $P2_1/n$, $a = 14.229$ (3) Å, $b = 22.683$ (6) Å, $c = 15.913$ (4) Å, $\beta = 98.92°$ (2), $Z = 4$. The copper(II) stereochemistries are close to trigonal bipyramidal with the alkoxide taking an equatorial bridging site. The nitrite ligand is asymmetrically bound, forming an O,N bridge between axial sites. Despite very close structural similarity to the ferromagnetic acetate complex ($2J = +24$ cm^{-1}), the nitrite complex is quite strongly antiferromagnetically coupled ($2J = -278$ cm^{-1}). This is traced to complementary symmetries of the bridging ligand orbitals. This concept of *ligand orbital complementarity* is also used to gain a deeper understanding of the diamagnetism of the azide complex $[Cu_2(L-Et)(N_3)]^{2+}$. The relationship of these findings to the geometry and magnetic properties of methemocyanin and oxyhemocyanin is discussed.

Introduction

Although there is already a long history and a prolific literature on the subject of magnetic coupling in binuclear copper(II) complexes,[3-7] a sustained interest remains.[8] In part, this is because binuclear copper sites in proteins such as hemocyanin and laccase[9] are notable examples of what still comprises only a handful of complexes[10-14] that closely approach diamagnetism at room temperature. On the synthetic front, new series of complexes that

mimic the protein sites or relate the extent of magnetic coupling to detailed structural parameters continue to be discovered.[14-23] And at the same time, the conceptual understanding of magnetic coupling in terms of the interactions of magnetic orbitals continues to evolve.[24-27] Unsymmetrically dibridged systems are, however, poorly understood.

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We were attracted to this area by the problem of preparing credible synthetic models for the oxygen-carrying copper protein hemocyanin. In a recent paper[16] we showed that all of the structural, spectroscopic, and magnetic properties of the azidomet form of hemocyanin could be reproduced in the complex $[Cu_2-(L-Et)(N_3)]^{2+}$, where HL-Et is the binucleating ligand $N,N,-N',N'$-tetrakis(2-(1-ethylbenzimidazolyl))-2-hydroxy-1,3-diaminopropane:
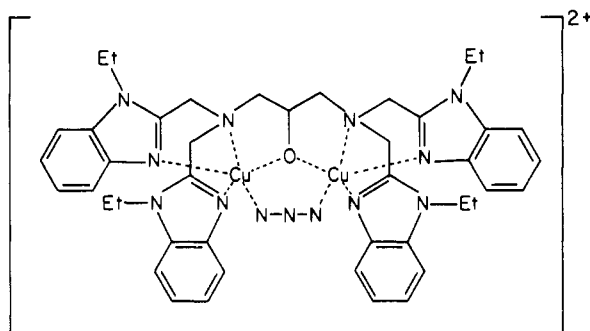
Notably, the azide complex was found to be fully diamagnetic at room temperature.[28] At the same time, it was found that replacement of the azide ion by acetate, pyrazolate, nitrite, etc. produced compounds of identical composition, $[Cu_2(L-Et)X]^{2+}$ (where $X^- = OAc^-$, pyz^-, NO_2^-, etc.), but of widely varying magnetic properties. The acetate complex is a weak ferromagnet $(2J \simeq +24 \text{ cm}^{-1})$,[29] the pyrazolate is a weak antiferromagnet, and the nitrite is a moderate antiferromagnet $(2J \simeq -278 \text{ cm}^{-1})$, all contrasting sharply with the azide $(|-2J| > 1100 \text{ cm}^{-1})$. How such similar complexes could display such different magnetic properties was not at all obvious. Knowing that the answer must lie in the details of their structures led us to choose the two most dissimilar complexes for X-ray structure determination. These were the weakly ferromagnetically coupled acetate and the fully antiferromagnetically coupled, diamagnetic azide. It turned out that the acetate and azide complex structures differed substantially in their coordination stereochemistries. The acetate approximates a trigonal bipyramid while the azide is closer to a tetragonal pyramid. This led us to propose that the different magnetic properties arose from different ground states, d_{z^2} for the acetate and $d_{x^2-y^2}$ for the azide. As a result, the overlap of their magnetic orbitals fully exploited the excellent exchange-mediating properties of the bridging alkoxide ligand in the azide complex but not in the acetate complex. We now refer to this phenomenon as *orbital switching*.[30]

To further test this theory, we decided to determine the X-ray structure of the nitrite derivative, $[Cu_2(L-Et)(NO_2)][ClO_4]_2$. Its intermediate degree of antiferromagnetic coupling suggested the possibility of a structure intermediate between that of the acetate and the azide. There was, however, no really good reason to expect that a gradual change of magnetic properties would correlate with a gradual change of structure between the two limiting ideal stereochemistries of five-coordination. In fact, the nitrite complex turns out to be structurally very similar to the previously determined acetate derivative whose coordination stereochemistry is close to trigonal bipyramidal. At first glance this finding might appear to be inconsistent with the predictions of the orbital-switching hypothesis. However, a subtlety of the magnetic coupling mechanism in unsymmetrical dibridged systems is revealed. The coupling involves an unusually strong d_{z^2} interaction mediated by the bridging nitrite.

Surprisingly little is known about the magnetic exchange-mediating properties of the μ-nitrito ligand. In the only known

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(29) Quoted values of the exchange parameter are derived from the $-2J$ form of the spin Hamiltonian $H = -2J\vec{S}_1 \cdot \vec{S}_2$. Thus, $2J$ represents the singlet/triplet splitting.

(30) This term is closely related to the term *orbital reversal* coined by Kahn.[26]

empirical formula	$C_{13}H_{19}N_{11}O_{11}Cl_2Cu_2$
fw	1093.9
space group	$P2_1/n$, monoclinic
a, Å	14.229 (3)
b, Å	22.683 (6)
c, Å	15.913 (4)
β, deg	98.92 (2)
V, Å^3	5073 (2)
Z	4
λ (Mo Kα), Å	0.710 69
μ, cm^{-1}	10.10
index ranges	
h	0–14
k	0–22
l	–16 to +16
no. of reflcns measd	5343
no. of unique reflcns	4755
no. of reflcns used having $I > 2[\sigma(I)]$	2659
R	0.076
R_w	0.075

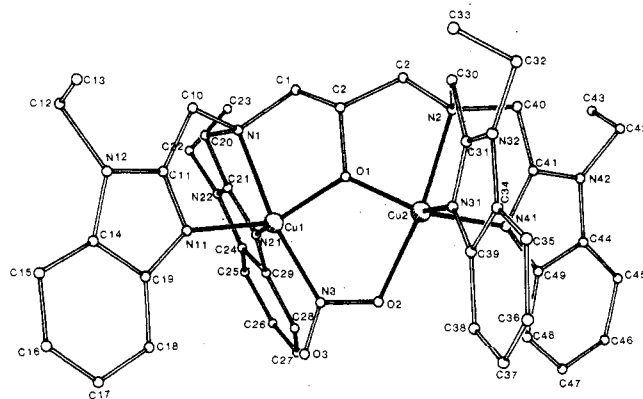**Figure 1.** Atom-numbering scheme for the cation $[Cu_2(L-Et)(NO_2)]^{2+}$.

example of a dimeric complex, the nickel(II) species $[Ni(en)_2-(NO_2)]_2^{2+}$, which has nitrite in a single O atom bridging mode, magnetic coupling is modest in magnitude and antiferromagnetic in nature $(2J = -29 \text{ cm}^{-1})$.[31] Closely related polymeric systems, which have the same unsymmetrical two-atom O,N-bridging mode found in the present work, have similar modest interactions $(|-2J| \leq 33 \text{ cm}^{-1})$.[32,33] The present complex shows an interaction almost 10 times stronger.

Another reason for investigating the present structure was to determine the coordination mode of the nitrite ion. A symmetrical 1,3-bridging mode, as would seem to be structurally quite feasible in view of the three-atom bridging mode found for both the acetate and azide analogues, has never been observed in a μ-nitrito complex.[34]

Finally, nitrite is a ligand for methemocyanin, half-methemocyanin, and possibly dimer hemocyanin.[35] It is of interest to learn how nitrite interacts with binuclear copper species particularly from the viewpoints of structure and magnetic coupling. Since it is a potential two-atom bridging ligand like dioxygen, some of its properties may also be relevant to oxyhemocyanin.

Experimental Section

The nitrite complex $[Cu_2(L-Et)(NO_2)][ClO_4]_2$ was prepared as previously described.[16] Green single crystals were grown from acetonitrile by diethyl ether vapor diffusion. An irregularly shaped crystal of ap-

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Table II. Atom Coordinates (×10⁴) and Temperature Factors (×10³)ᵃ

atom	x	y	z	U, Å²
Cu(1)	3685 (1)	6953 (1)	6204 (1)	47 (1)*
Cu(2)	4234 (1)	7072 (1)	4256 (1)	53 (1)*
O(1)	4158 (8)	6669 (4)	5251 (6)	99 (5)*
N(1)	3889 (7)	6084 (4)	6629 (6)	43 (4)*
N(2)	4803 (7)	6274 (4)	3873 (6)	48 (4)*
C(1)	4610 (10)	5854 (5)	6139 (8)	64 (6)*
C(2)	4293 (13)	6063 (7)	5212 (8)	86 (8)*
C(3)	5033 (11)	5939 (6)	4695 (8)	73 (7)*
C(10)	2952 (9)	5765 (5)	6458 (8)	56 (6)*
C(11)	2188 (9)	6219 (7)	6480 (8)	51 (6)*
N(11)	2334 (8)	6781 (5)	6450 (6)	46 (5)*
N(12)	1271 (8)	6067 (5)	6518 (7)	64 (5)*
C(12)	852	5426	6580	161 (13)*
C(13)	579	5248	5901	272
C(14)	749 (10)	6597 (7)	6461 (9)	61 (6)*
C(15)	-232 (10)	6707 (7)	6455 (10)	82 (7)*
C(16)	-472 (11)	7287 (7)	6373 (10)	89 (8)*
C(17)	185 (10)	7734 (7)	6377 (9)	78 (7)*
C(18)	1152 (9)	7619 (6)	6392 (7)	51 (6)*
C(19)	1432 (9)	7034 (6)	6452 (8)	48 (5)*
C(20)	4233 (9)	6099 (5)	7557 (7)	48 (5)*
C(21)	4718 (9)	6675 (6)	7815 (7)	48 (5)*
N(21)	4530 (7)	7147 (4)	7337 (6)	42 (4)*
N(22)	5291 (8)	6771 (5)	8573 (6)	54 (5)*
C(22)	5591 (11)	6322 (7)	9207 (9)	81 (7)*
C(23)	6465 (12)	6016 (8)	9091 (11)	131 (10)*
C(24)	5519 (10)	7380 (6)	8557 (8)	58 (6)*
C(25)	6108 (9)	7706 (7)	9171 (8)	68 (6)*
C(26)	6198 (12)	8287 (7)	8933 (12)	85 (8)*
C(27)	5724 (10)	8540 (7)	8173 (11)	70 (7)*
C(28)	5157 (9)	8189 (5)	7600 (8)	52 (6)*
C(29)	5054 (8)	7593 (5)	7797 (7)	41 (5)*
C(30)	4082 (9)	5977 (5)	3246 (8)	54 (6)*
C(31)	3455 (9)	6460 (6)	2779 (8)	47 (5)*
N(31)	3371 (7)	6968 (4)	3117 (6)	52 (4)*
N(32)	2924 (8)	6374 (5)	2014 (7)	63 (5)*
C(32)	2855 (11)	5853 (7)	1459 (10)	99 (8)*
C(33)	2053 (21)	5473 (8)	1608 (16)	241 (19)*
C(34)	2462 (10)	6911 (7)	1828 (8)	59 (6)*
C(35)	1858 (11)	7108 (8)	1113 (10)	79 (8)*
C(36)	1591 (11)	7687 (9)	1129 (10)	82 (8)*
C(37)	1904 (10)	8064 (6)	1785 (9)	64 (6)*
C(38)	2462 (9)	7865 (6)	2489 (10)	54 (6)*
C(39)	2753 (9)	7281 (6)	2526 (7)	49 (5)*
C(40)	5662 (10)	6400 (6)	3515 (9)	65 (6)*
C(41)	5980 (10)	7021 (7)	3703 (8)	53 (6)*
N(41)	5414 (7)	7431 (4)	3889 (6)	53 (4)*
N(42)	6853 (8)	7235 (5)	3604 (7)	63 (5)*
C(42)	7704 (13)	6900 (8)	3399 (12)	96 (9)*
C(43)	8361 (12)	6747 (8)	4195 (11)	127 (10)*
C(44)	6864 (14)	7832 (7)	3766 (8)	65 (7)*
C(45)	7527 (13)	8393 (10)	3795 (11)	94 (9)*
C(46)	7209 (21)	8844 (9)	3985 (12)	110 (13)*
C(47)	6300 (18)	8944 (10)	4119 (11)	98 (10)*
C(48)	5638 (12)	8507 (8)	4100 (9)	74 (8)*
C(49)	5958 (13)	7945 (7)	3929 (9)	60 (7)*
N(3)	3525 (8)	7710 (5)	5607 (8)	73 (5)*
O(2)	3704 (8)	7770 (4)	4816 (7)	98 (5)*
O(3)	3271 (12)	8129 (7)	5838 (10)	109 (8)*
O(3')	3573 (23)	8234 (15)	4573 (21)	82 (13)*
Cl(1)	7544 (3)	5253 (2)	5848 (3)	78 (2)*
O(11)	7282 (13)	5403 (7)	4990 (12)	193 (11)*
O(12)	7798 (9)	4658 (5)	5852 (9)	136 (7)*
O(13)	8219 (11)	5582 (8)	6202 (13)	230 (12)*
O(14)	6723 (8)	5321 (5)	6230 (9)	126 (7)*
Cl(2)	6125 (6)	5425 (2)	1619 (4)	110 (3)*
O(21)	5508 (20)	5297 (8)	2166 (15)	177 (15)*
O(22)	6158 (17)	4980 (8)	1014 (13)	114 (11)*
O(23)	6002 (20)	5966 (7)	1353 (14)	168 (15)*
O(24)	7099 (26)	5462 (23)	2153 (26)	299 (29)*
O(21')	5035 (46)	5502 (21)	1133 (47)	274 (47)*
O(22')	6554 (40)	5891 (25)	1336 (33)	200
O(23')	6160 (60)	5251 (31)	2462 (43)	211 (43)*
O(24')	6795 (30)	5020 (21)	1406 (32)	169 (19)

ᵃ An asterisk denotes the equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VIII. Bond Lengths (Å) and Bond Angles (deg) about the Copper Atoms

Cu(1)···Cu(2)	3.325 (2)	Cu(1)-O(1)-Cu(2)	127.1 (5)
Cu(1)-O(1)	1.87 (1)	Cu(2)-O(1)	1.85 (1)
Cu(1)-N(1)	2.09 (1)	Cu(2)-N(2)	2.11 (1)
Cu(1)-N(11)	2.06 (1)	Cu(2)-N(31)	2.04 (1)
Cu(1)-N(21)	2.06 (1)	Cu(2)-N(41)	2.03 (1)
Cu(1)-N(3)	1.96 (1)	Cu(2)-O(2)	2.02 (1)
O(1)-Cu(1)-N(1)	83.6 (4)	O(1)-Cu(2)-N(2)	84.3 (4)
O(1)-Cu(1)-N(11)	123.7 (4)	O(1)-Cu(2)-N(31)	126.7 (4)
O(1)-Cu(1)-N(21)	123.4 (5)	O(1)-Cu(2)-N(41)	127.3 (5)
O(1)-Cu(1)-N(3)	86.2 (5)	O(1)-Cu(2)-O(2)	86.2 (5)
N(1)-Cu(1)-N(11)	81.1 (4)	N(2)-Cu(2)-N(31)	81.4 (4)
N(1)-Cu(1)-N(21)	83.4 (4)	N(2)-Cu(2)-N(41)	83.8 (4)
N(1)-C1(1)-N(3)	169.6 (5)	N(2)-Cu(2)-O(2)	170.4 (5)
N(11)-Cu(1)-N(21)	108.1 (4)	N(31)-Cu(2)-N(41)	101.7 (4)
N(11)-Cu(1)-N(3)	103.0 (5)	N(31)-Cu(2)-O(2)	105.5 (5)
N(21)-Cu(1)-N(3)	104.1 (5)	N(41)-Cu(2)-O(2)	101.1 (5)

proximate dimensions 0.20 × 0.17 × 0.23 mm was used for the structure determination. Intensity data were collected at room temperature on a Nicolet R3m diffractometer using graphite-monochromated Mo Kα radiation. The cell parameters were obtained by least-squares refinement of 25 accurately centered reflections (18° < 2θ < 22°). By the use of the θ-2θ technique and variable scan rates (3.66-29.3° min⁻¹), a total of 5343 reflections were collected in the range 3° < 2θ < 40°. There were very few reflections above background beyond the 40° limit because of the small size and weak diffracting power of the crystal. Crystal stability was monitored by recording 3 standard reflections every 100 measurements, and no significant variation was observed. Data reduction gave 4755 unique reflections of which 2659 having $I > 2$ [$\sigma(I)$] were used in the structure determination. Intensities were corrected for Lorentz-polarization effects, and an empirical absorption correction was applied on the basis of ψ-scan data (transmission factors varied from 0.806 to 0.870). Systematic absences uniquely specified the space group as $P2_1/n$. Crystal data are summarized in Table I.

The two independent copper atoms were located by using Patterson calculations, and the remaining non-hydrogen atoms were found from difference Fourier maps and blocked-cascade least-squares refinement to give a conventional R of 0.17. Hydrogen atoms were included at calculated positions by using a riding model with C–H = 0.96 Å and the hydrogen thermal parameters fixed at 1.2 times the equivalent isotropic U of their carrier atoms.

One of the perchlorate ions was found to be severely disordered and was modeled as a twofold disorder. Attempts to apply more complex models did not improve the fit. In addition, one of the ligand's ethyl substituents (C12 - C13) did not refine. These two atoms were fixed in positions found from difference Fourier maps. The NO_2^- ligand showed 70:30 disorder between the configurations: Cu(1)-N(O(3))-O-Cu(2) and Cu(1)-O-N(O(3'))-Cu(2). The site occupancy factors of O(3) and O(3') were refined subject to the condition that their sum equal unity. N(3) and O(2) were refined in the 70% orientation only, this did not introduce any noticeable anomalies in bond lengths or thermal parameters. The atom-numbering scheme is shown in Figure 1.

Anisotropic refinement of all non-hydrogen atoms except those showing disorder resulted in a conventional $R = 0.0764$, $R_w = 0.075$ where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and $w = [\sigma^2(F_o) + 0.0017F_o^2]^{-1}$. A final difference map showed no significant features. The programs used for data reduction and structure solution are included in the SHELXTL (version 4.0) package.[36]

Final atomic coordinates and temperature factors for the non-hydrogen atoms are listed in Table II. Complete listings of bond lengths and bond angles are given in Table III and Table IV, respectively, in the supplementary data, while a list of important bond lengths and angles is given in Table VIII. A listing of anisotropic thermal parameters for the non-hydrogen atoms is given in Table V in the supplementary data. Hydrogen atom coordinates and temperature factors are given in Table VI in the supplementary material. Final observed and calculated structure factors are given in Table VII (16 pages) of the supplementary material. A stereoscopic packing diagram is included in the supplementary data (Figure 2).

Results and Discussion

Nitrite Coordination. The mode of coordination of the NO_2^- ion would, under normal circumstances, be identifiable by IR

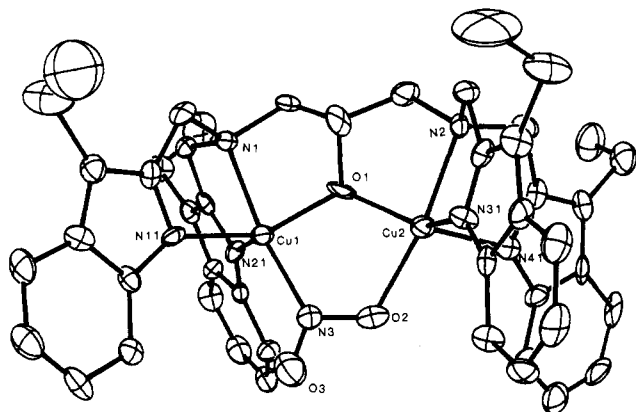(36) Sheldrick, G. M. "SHELXTL User Manual, Revision 4"; Nicolet XRD Corp.: Madison, WI.

Figure 3. Perspective view of the cation $[Cu_2(L\text{-}Et)(NO_2)]^{2+}$ showing the major orientation of the nitrite bridging ligand. Thermal elipsoids are at 20% probability.

Figure 4. Perspective diagram of the inner coordination sphere of $[Cu_2(L\text{-}Et)(NO_2)]^{2+}$.

criteria.[34] However, in the present complex the nitrite stretching frequencies are virtually completely masked by absorptions of the binucleating ligand L-Et. The as yet unobserved *three*-atom, symmetrical O,O-bridging mode would seem to be geometrically feasible in view of the three-atom acetate and azide bridges found in our earlier work,[16] but the X-ray structure (Figure 3) reveals the *two*-atom, unsymmetrical O,N-bridging mode of coordination that is most commonly found in μ-nitrito complexes.[34] A possible electronic reason why the two-atom bridge is favored over the three-atom bridge arises from the idea of orbital complementarity in the bridging ligands, discussed at greater length below. In brief, the other bridging ligand, alkoxide, dictates that antisymmetric lobes of the nitrite σ-bonding HOMO are favored over symmetric lobes for maximizing overlap of the copper magnetic orbitals. The a_1 symmetry of the nitrite HOMO[37] determines that antisymmetric lobes are available in the 1,2-bridging mode but not in the 1,3-bridging mode.

Throughout our synthetic work with the present L-Et ligand we have been unable to synthesize any dibridged complexes of the type $[Cu_2(L\text{-}Et)(X)]^{2+}$ having X^- in a *single*-atom bridging mode. A 1,1-bridging mode of coordination is known for the nitrite ion.[31] Its nonoccurrence in the present work is almost certainly a consequence of the five-membered chelate ring size of the alkoxide/amine backbone of L-Et. Judging from systems where valid comparisons to six-membered ring chelates can be made[14] the 1,1-bridging mode would not be possible unless the chelating rings were expanded to at least six atoms.

The dimensions of the nitrito group cannot be discussed in great detail because of the 70:30 disorder with respect to O,N interchange. However, we have no reason to believe they differ significantly from the reported average values.[34] The bridging bond N(3)–O(2) has a length of 1.325 (17) Å.

It is of interest to note the Cu···Cu separation of 3.325 (2) Å. As expected, it is shorter than the 3.46- and 3.66-Å Cu···Cu separations observed in the analogous three-atom-bridged acetate and azide complexes[16] and longer than the $\sim$3.1 Å separations found in one-atom-dibridged systems.[4] The present work gives expectation values for nitritomethemocyanin although the difference in stereochemistry between the present complex (trigonal bipyramidal) and methemocyanin (probably tetragonal) must be taken into account. The 0.20-Å difference in Cu···Cu separation between the trigonal-bipyramidal acetate complex and the tetragonal azide complex[16] can be partitioned into two parts: (a) the 0.09-Å difference in the acetate and azide "bite" sizes,[38] and (b) the remaining 0.10-Å difference, ascribed to the increase in Cu···Cu separation upon going to the more sterically crowded tetragonal stereochemistry. Thus, our estimate of the Cu···Cu separation in nitritomethemocyanin is about 0.10 Å longer than
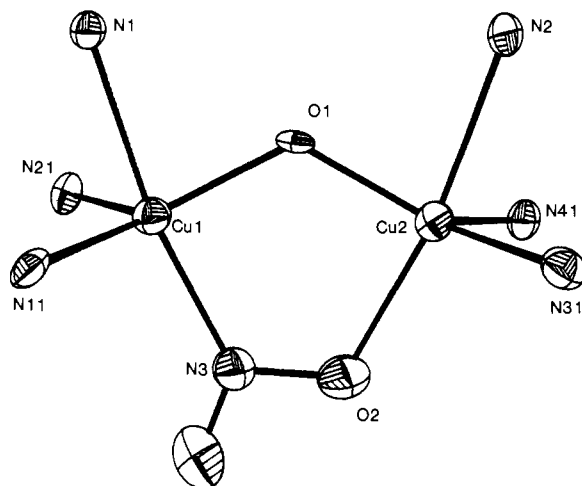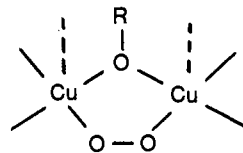
the present complex, i.e. 3.43 Å. Of more interest, however, is to follow this reasoning through to oxyhemocyanin, the most important of the presumed two-atom-bridged species, where Cu···Cu separations have in fact been measured by EXAFS.[39,40] A tetragonal, dibridged structure

$$\text{Cu} \underset{\underset{\displaystyle O-O}{\diagdown \diagup}}{\overset{\underset{\displaystyle R}{\overset{\displaystyle |}{O}}}{\diagup \diagdown}} \text{Cu}$$

is most likely.[16] Adding the "bite" increase of peroxide over nitrite (approximately $1.45 - 1.32 = 0.13$ Å) to the observed Cu···Cu distance in the nitrite complex (3.325 Å) and then adding an additional 0.10 Å because of the stereochemical change bring the estimate for oxyhemocyanin to about 3.55 Å. This value lies within the measured range of 3.55–3.66 (2) Å[39,40] and, thus, lends some additional credence to the proposed active-site structure of oxyhemocyanin.

Copper Stereochemistry. The coordination stereochemistry is shown in Figure 4. Both copper(II) atoms are essentially trigonal bipyramidal (TBP) with the nitrite and tertiary amine ligands in the axial positions. Inspection of the bond angles in Table VII shows that Cu(1) has no angles that differ from TBP ideality by more than 14°. Most are within 9°. Cu(2) is slightly more distorted, but no angles differ from TBP ideality by more that 19° and most are again within 9°. There is no evidence of any distortion toward a tetragonal stereochemistry as was so marked in the corresponding azide structure.[16] The pairs of equatorial Cu–N(benzimidazole) bond lengths are identical within experimental error (Table VII). They are numerically within experimental error of those in the analogous acetate complex,[16] which in all respects has a very similar structure. Perhaps the biggest difference in these two structures is the Cu···Cu separation: 3.325 (2) Å in the nitrite and 3.459 (2) Å in the acetate. This is clearly a consequence of the shorter, two-atom bridge in the former. But it is interesting to note that this contraction occurs almost entirely at the expense of the Cu–O(alkoxide) bond lengths rather than the alkoxide Cu–O–Cu bond angle. They shorten from 1.89 (1) and 1.92 (1) Å in the acetate[16] to 1.85 (1) and 1.87 (1) Å in the nitrite while the Cu–O–Cu angle decreases only $\sim$3° from 130.6 (5) to 127.1 (5)°. This shortening of the Cu–O(alkoxide) bonds in the nitrite complex may contribute to its greater magnetic coupling in the nitrite relative to that in the acetate. The two perchlorate counterions do not interact with the copper complex

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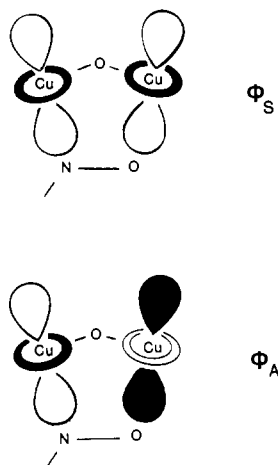
Figure 5. Symmetric and antisymmetric combinations of the d_{z^2} magnetic orbitals.
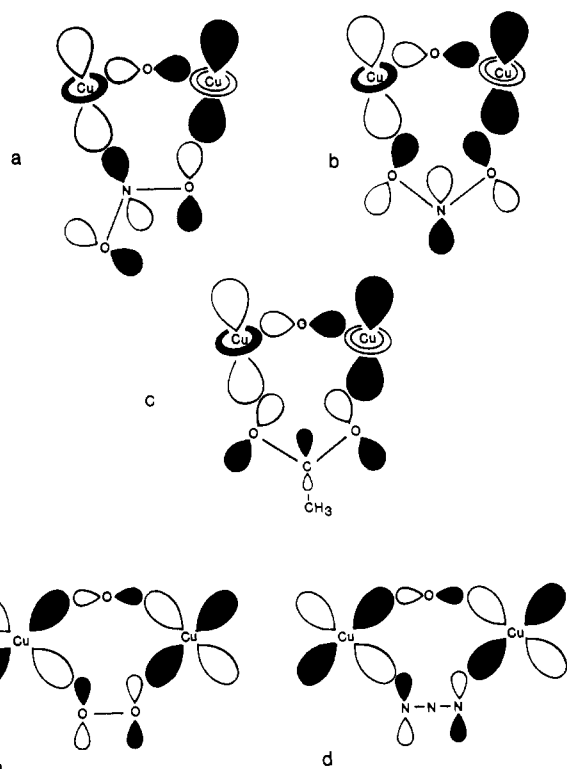

Figure 6. Bridging ligand orbital complementarity and noncomplementarity for various dibridged systems: (a) complementarity of alkoxide/1,2-nitrite; (b) noncomplementarity of alkoxide/1,3-nitrite; (c) noncomplementarity of alkoxide/acetate; (d) complementarity of alkoxide/azide; (e) complementarity of RO⁻/peroxide. Only the antisymmetric combination of copper magnetic orbitals is illustrated.

in any significant way. There are no perchlorate oxygen atoms closer than 2.3 Å to any hydrogen atoms of L-Et.

Magnetostructural Correlations. The close to trigonal-bipyramidal stereochemistry of the d^9 copper(II) atoms in the present dimer leaves little doubt that they have $(d_{z^2})^1$ ground states. Conventional wisdom would suggest that the major σ pathway for the interaction of these *magnetic orbitals* (i.e. the orbitals containing the unpaired electrons)[26] would involve the nitrite ligand, which bridges the major, prolate lobes of the d_{z^2} orbitals. It is counterintuitive then, on two counts, that the extent of antiferromagnetic coupling is so large in the present complex ($2J$ = -278 cm⁻¹). Strong antiferromagnetic coupling in copper dimers is typically a feature of $d_{x^2-y^2}$ ground states, and to our knowledge the only complex having comparably large coupling via d_{z^2} magnetic orbitals is the axially bridged μ-hydroxy complex $[Cu_2(OH)(bpy)_4]^{3+}$ (bpy = 2,2'-bipyridine),[25] where $2J$ = -322 cm⁻¹. Bridging hydroxide ion in this and related species having large obtuse Cu-O-Cu angles (130–140°) is now recognized to be an extremely good mediator of antiferromagnetic coupling, but the limited data on the 1,2-bridging nitrite ion ($|-2J|$ < 33 cm⁻¹)[31-33] do not suggest that it can mediate such strong d_{z^2} coupling on its own. We therefore look to the equatorial alkoxide ligand for a possible role, remembering that it too bridges the copper centers, and, moreover, it provides a σ pathway for interaction of the "donut" lobes of the d_{z^2} magnetic orbitals. Both this equatorial donut orientation via the alkoxide and the axial prolate orientation via the nitrite are illustrated in Figure 5.

Strong antiferromagnetic interactions arise in any dimer when the symmetric (ϕ_S) or antisymmetric (ϕ_A) combinations of the two magnetic orbitals differ significantly in energy.[24] These combinations are illustrated for d_{z^2} orbitals in Figure 5. It does not matter which combination is lower in energy, only that they are reasonably different. When this is the case, the spin-paired S = 0 state will be lower than the S = 1 state. If on the other hand the ϕ_A and ϕ_S combinations are accidentally equal in energy, or nearly so, then the S = 1 state can become lower in energy than the S = 0 state. This is ferromagnetism. The clue to understanding which situation will prevail lies in the relative interaction of ϕ_A and ϕ_S with the highest filled orbitals of the bridging groups. Usually, a simple inspection of the symmetry of the highest occupied molecular orbital (HOMO) of the bridging ligand is sufficient.[24,26] For the present complex these are assumed to be a 2p orbital on the alkoxide and the $6a_1$ orbital on the nitrite.[37,31] The interactions of these filled ligand orbitals with the metal d_{z^2} orbitals are, of course, antibonding,[24] and they are illustrated in Figure 6a for the antisymmetric combination. The important observation is that *both* ligand HOMOs have the correct symmetry for antibonding overlap with the antisymmetric combination of d_{z^2} orbitals. Thus, both ligands provide orbital interaction pathways that act in concert to make ϕ_A different in energy from ϕ_S. We shall call this phenomenon *ligand orbital complementarity*. It has been recognized by Kida,[17] who recently

synthesized a series of copper(II) dimers with unusually low magnetic coupling despite well-oriented $d_{x^2-y^2}$ magnetic orbitals. *Non*complementarity of the ligand HOMOs was invoked to rationalize this observation. To illustrate such noncomplementarity in the present system let us consider the hypothetical 1,3-bridged nitrite complex in Figure 6b. Inspection of the overlap symmetries shows that the alkoxide has the correct symmetry to overlap (in the antibonding sense) with ϕ_A, but the 1,3-nitrite has no net overlap. Not illustrated is the overlap of the same ligand orbitals with ϕ_S. But, it is easy to see that, in this case, the situation is reversed. Nitrite would have the correct symmetry while alkoxide would have no net overlap. As a consequence, alkoxide and nitrite are trying to stabilize different combinations of the metal orbitals. Less energy difference in ϕ_A and ϕ_S will result, and weaker antiferromagnetism will be observed. In fact, if the two ligands have similar but opposite effects, it is possible that ϕ_A and ϕ_S will become approximately equal in energy. In such a case, ferromagnetism will be observed. Exactly this situation seems to exist in the acetate derivative, where $2J$ = +24 cm⁻¹. In Figure 6c the acetate a_1 HOMO[24] is illustrated to show its noncomplementarity with alkoxide. It is likely that the near equivalence of ϕ_A and ϕ_S (and hence the ferromagnetism) arises because of an accidental balancing of effects. The strongly mediating alkoxide interacts with the minor, donut lobes of the d_{z^2} orbitals whereas the more weakly mediating acetate interacts with the major, prolate lobes.

Similar arguments can also be applied to our azide complex, which has interacting $d_{x^2-y^2}$ magnetic orbitals via an alkoxide and an 1,3-azide bridge.[16] The complex is very strongly antiferromagnetically coupled (diamagnetic). It is not surprising therefore to find that viewing the ligand orbitals in the manner of Kida[17] reveals complementarity. This is illustrated in Figure 6d. The strong mediating properties of the alkoxide are augmented by those of the azide.

Conclusion

The present investigation supports the basic hypothesis[16] that bridge mediation of $d_{x^2-y^2}$ interactions is a major reason why the tetragonal azide complex $[Cu_2(L\text{-}Et)(N_3)]^{2+}$ can attain complete

diamagnetism. Orbital switching from $d_{x^2-y^2}$ to d_{z^2} magnetic orbitals explains the lower magnitude of magnetic coupling in related complexes. However, a comparison of acetate and nitrite complexes, which differ magnetically much more than might be expected on the basis of their isostructural d_{z^2} interactions, reveals a more subtle effect of orbital symmetry complementarity in the HOMOs of bridging ligands. This concept of orbital of complementarity and noncomplementarity should prove to be a general consideration in multibridged magnetically interacting systems and a particular consideration in unsymmetrical dibridged copper(II) dimers where magnetic coupling phenomena are not so well understood.[22,23,41] We note that in the proposed structure for oxyhemocyanin the RO⁻ and O_2^{2-} bridging ligands do indeed have complementary orbital symmetries. They are the 2p orbital on oxygen and the π_g^* of O_2^{2-}. Their complementary antibonding overlap with the antisymmetric combination of $d_{x^2-y^2}$ orbitals is illustrated in Figure 6e. The diamagnetism of oxyhemocyanin is no longer surprising when viewed in this light.

These magnetic arguments as well as structural ones based on the dimensions of the bridging ligands continue to support the present structural model[39,16] for oxyhemocyanin and the credibility of $[Cu_2(L-Et)(N_3)]^{2+}$ as a model for methemocyanin.

Supplementary Material Available: Tables of bond lengths and angles (Tables III and IV), anisotropic temperature factors (Table V), hydrogen coordinates (Table VI), and observed and calculated structure factors (Table VII) and a unit cell packing diagram (Figure 2) (22 pages). Ordering information is given on any current masthead page.

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Transition-Metal Coordination Compounds of a Tripodal Tetradentate Pyrazole Derivative. X-ray Structure of the Dimer [Aqua(tris((3,5-dimethylpyrazol-1-yl)methyl)amine)cobalt(II)][fluoro(tris((3,5-dimethyl-pyrazol-1-yl)methyl)amine)cobalt(II)] Tris(tetrafluoroborate)–1.5-Ethanol

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The synthesis and characterization of transition-metal coordination compounds containing the newly synthesized ligand tris-((3,5-dimethylpyrazol-1-yl)methyl)amine (abbreviated amtd) are described. The tetrafluoroborate compounds, which are all dimers, have the general formula $M_2(amtd)_2F(BF_4)_3(EtOH)_x(H_2O)_y$ (M = Co, Cu, Zn; x = 0–1.5; y = 1–2), $Ni_2(amtd)_3(BF_4)_4(H_2O)_2$, and $Ni_2(amtd)_2F_2(BF_4)_2(EtOH)_{0.5}$. The fluorides are formed upon tetrafluoroborate decomposition. The nitrate compounds have the general formula $M(amtd)(NO_3)_2$ (M = Co, Ni, Cu, Zn). The chloride and thiocyanate compounds have the general formula $[M(amtd)X]_2(MX_4)(EtOH)_x(H_2O)_y$ (M = Co, Cu, Zn; X = Cl, NCS; x = 0.5–1; y = 0–1.5) and $Ni(amtd)X_2(H_2O)_x$ (X = Cl, NCS; x = 0–1.5). In all compounds amtd acts as a chelating tripodal tetradentate ligand. In the cases of Co, Cu, and Zn also one counterion (F, monodentate NO_3, Cl, or NCS) is coordinated to the metal ion, resulting in five-coordination. Octahedrally based six-coordination is found in all Ni(II) cases, with two counterions (F, Cl, or NCS) or one bidentate nitrate ion bound to the nickel ion. Six nitrogen atoms donated by two ligands in the case of $Ni_2(amtd)_3(BF_4)_4(H_2O)_2$ yield a distorted-octahedral geometry. The ligand field spectra of the nickel compounds are typical for six-coordination. In the case of five-coordination (M = Co, Cu, Zn; anion = BF_4, NO_3, Cl, NCS) the coordination geometry is distorted trigonal bipyramidal. This is deduced from the X-ray structure determination of the cobalt tetrafluoroborate compound, the ligand field spectra of Co(II), the EPR spectrum of a cobalt-doped zinc tetrafluoroborate compound, the EPR spectra of Cu(II), and isomorphism within the group of compounds with the same anion. A crystal of $[Co_2(amtd)_2F(H_2O)(EtOH)](BF_4)_3(EtOH)_{0.5}$ was used in a structure determination: monoclinic, space group $P2_1/n$, a = 29.312 (9) Å, b = 11.822 (7) Å, c = 14.244 (7) Å, β = 103.41 (3)°, Z = 4, and T = –162 °C. The structure was solved by heavy-atom techniques and refined by least-squares methods to a residual R value of 0.055 (R_w = 0.078). The coordination geometry of both cobalt atoms in this dimer is five-coordinated distorted trigonal bipyramidal. A fluoride ion and a water molecule are coordinated respectively to the cobalt ions (Co–F = 1.902 (5) Å, Co–O = 2.032 (6) Å). The Co–Co distance is 6.254 (2) Å. The amtd ligands are coordinated identically to both cobalt ions. The two cobalt to amine nitrogen distances are 2.30 Å, and the six cobalt to pyrazole nitrogen distances are about 2.03 Å. The bridge in this dimer is built up from the coordinated fluoride ion, an ethanol molecule, and the coordinated water molecule, which are linked to one another by hydrogen bonds.

Introduction

The increasing interest in chelating polydentate nitrogen-donor ligands, especially heterocyclic compounds, is based on the occurrence of such systems in nature.[1] Most attention is given to model systems containing imidazoles, benzimidazoles, and pyridines.[2-4] Attention is also paid to pyrazole derivatives,[5,6] because of the similarity of pyrazoles and imidazoles. A large variety of pyrazole derivatives can now be prepared through a novel method for the synthesis of N-substituted pyrazole chelates.[7-9] The

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