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Synthesis, Crystal Structure, and Magnetic Properties of a Pyrazolate-Bridged Binuclear Copper(II) Complex

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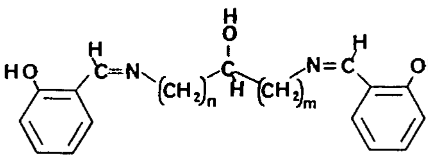
A new pyrazolate-bridged binuclear Cu(II) complex, $[LCu_2(prz)]$ (**2**), where prz is the monoanion of pyrazole and L^{3-} is the trianion of the Schiff-base ligand formed from the condensation of 2 mol of salicylaldehyde and 1 mol of 1,4-diaminobutan-2-ol, is characterized by single-crystal X-ray diffraction techniques. Complex **2** crystallizes from a DMF solution in the space group $P2_1/c$ with dimensions $a = 11.813$ (6) Å, $b = 18.049$ (6) Å, $c = 9.680$ (4) Å, $\beta = 105.67$ (4)°, and $Z = 4$. The crystal structure of **2** shows a disordering of the carbon atom positions of the five- and six-membered chelate rings. A satisfactory model of the disorder was achieved by refining the disordered atoms in positions of 50% occupancy. Agreement factors of $R = 5.4\%$ and $R_w = 7.2\%$ were obtained after final cycles of anisotropic refinement of all non-hydrogen atoms. The magnetic susceptibility of complex **2** has been measured in the temperature range 297.5–5.0 K. The exchange coupling parameter, $2J$, was determined to be -545.6 cm^{-1} from least-squares fitting of the data. The magnetic properties of **2** have been compared with those reported recently for two structurally similar compounds.

Introduction

Magnetic properties of binuclear copper(II) complexes have been of interest for some time, and our understanding of the structural and electronic factors that govern magnetic exchange phenomena in these complexes continues to evolve.[4] In bis(μ-hydroxo)- and bis(μ-alkoxo)-bridged binuclear copper(II) complexes, Hatfield and Hodgson[5,6] have observed an increase in the strength of antiferromagnetic exchange coupling with increasing Cu–O–Cu bridging angle in the range 90–105°. More recently, interest in complexes containing larger bridging angles (120–135°) and unsymmetric doubly bridged structures has stimulated a closer look at the effect of structure and the nature of the bridging ligands on the strength of exchange interactions.[7] Single-oxo-bridged binuclear Cu(II) complexes are known[6-10] to show substantially larger antiferromagnetic exchange coupling compared to their symmetric doubly bridged counterparts. The strength of the exchange interaction can be either enhanced or attenuated depending on the presence of a second bridging ligand,[9] such as azide or acetate ions. This behavior has been reasonably well explained by using theories developed by Hoffmann et al.[11] and others.[12] In Hoffmann's treatment, the different bridging ligands can act in a complementary or countercomplementary fashion to enhance or attenuate the strength of the superexchange process as a result of difference in the symmetries of the magnetic orbitals.

McKee,[9] Mazurek,[10] and Nishida[13] and co-workers recently reported the structure and magnetic properties of several unsymmetric doubly bridged binuclear Cu(II) complexes. These complexes incorporate 1,3-diaminopropan-2-ol (structure Ia) and 1,5-diaminopentan-3-ol (structure Ib) moieties where the two Cu(II) ions are bridged by the deprotonated alkoxide oxygen atom and by another bridging ligand X^-. McKee[7] and Nishida[13] et al. utilized Hoffmann's theory of complementary and countercomplementary interactions to account for the observed strong antiferromagnetic exchange interactions.



Ia: $n = 1$, $m = 1$
b: $n = 2$, $m = 2$
c: $n = 2$, $m = 1$

Sinn et al.[14] reported the X-ray structures and magnetic exchange properties of several unsymmetric doubly bridged binuclear copper(II) complexes of the structural type Ic, where the backbone comprises the asymmetric 1,4-diaminobutan-2-ol moiety. Sin-

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Table I. Crystal Data

formula	$Cu_2O_3N_4C_{21}H_{20}$	$F(000)$	256
fw	503.50	cryst dimens, mm	0.25 × 0.40 × 0.50
space group	$P2_1/c$	μ, cm^{-1}	21.8
cryst system	monoclinic	R, R_w	0.054, 0.072
temp, K	295	no. of unique reflcns	2703
a, Å	11.813 (6)		
b, Å	18.049 (6)	no. of obsd reflcns	4562
c, Å	9.680 (4)	GOF	2.50
β, deg	105.67 (4)	radiation (λ, Å)	Mo Kα (0.71069)
V, $Å^3$	1987.1	data collcd	$\pm h,k,l$
Z	4	monochromator	graphite
d_{calcd}, g cm^{-3}	1.68 (1)	scan technique	$\omega - 2\theta$
d_{obsd}, g cm^{-3}	1.67	scan range, deg	0.6 + 0.340 tan ω

gle-atom X^- bridging ligands such as Cl^-, Br^-, OMe^-, or OH^- were used. We describe herein the synthesis, structure, and magnetic properties of a new pyrazolate- (prz-) bridged binuclear copper(II) complex, [LCu_2(prz)], which is of structural type Ic with X^- = pyrazolate. Hoffmann's theory of orbital complementarity has been applied in evaluating the magnetic properties of the copper complex.

Experimental Section

Physical Measurements. X-ray crystallographic data were obtained on an Enraf-Nonius CAD-4 diffractometer. Data reduction and solution of the structure were performed on a VAX-11/750 using the SDP package of programs.[15] Magnetic susceptibilities were obtained on a SQUID Series 800 VTS-50 susceptometer. Melting points were determined by using a Thomas Hoover capillary melting point apparatus and are reported as uncorrected values.

Reagents. All solvents used were either reagent or spectroscopic grade and were dried by conventional procedures prior to use. Reagents were used as received.

Synthesis of 1,4-Bis(salicylideneamino)butan-2-ol (H-L) (4). 1,4-Diamino-2-butanol dihydrochloride was synthesized according to a previously reported procedure.[16] A sample of 1,4-diamino-2-butanol dihydrochloride (0.7619 g, 4.3 mmol) dissolved in 20 mL of methanol was added to a solution of KOH (0.4829 g, 8.6 mmol) in 10 mL of methanol. The mixture was filtered, removing the NaCl precipitate, and the filtrate was added to salicylaldehyde (1.0635 g, 8.7 mmol). The yellow solution was stirred overnight in an open flask, after which the volume was reduced, yielding a yellow precipitate. The precipitate was filtered and washed with a small amount of methanol. The crude product was dissolved in acetonitrile and the resulting yellow solution decanted and allowed to evaporate, yielding bright yellow crystalline plates of 1,4-bis(salicylideneamino)butan-2-ol (0.6381 g, 47.5%; mp 148–150 °C).

Synthesis of [LCu_2(prz)] (2). A sample of **4** (0.1276 g, 0.408 mmol) in methanol (10 mL) was added dropwise to a stirred mixture containing pyrazole (0.0281 g, 0.413 mmol) and $Cu(NO_3)_2{\cdot}3H_2O$ (0.1994 g, 0.825 mmol) in methanol (25 mL). KOH (0.0925 g, 0.165 mmol) in methanol (10 mL) was added to the solution, forming a very dark purple precipitate. The pH was adjusted to 11.5 with additional methanolic KOH, and 5 mL of H_2O was added. The mixture was stirred and the precipitate collected and washed with water and methanol. Yield of crude complex was 0.1620 g (78.8%). Recrystallization from DMF afforded single crystals suitable for X-ray structure determination.

Collection and Reduction of X-ray Data. A red tabular crystal of **2** having approximate dimensions of 0.25 × 0.40 × 0.50 mm was mounted on a glass fiber with epoxy and used for data collection. Cell constants (Table I) and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 24 reflections measured by the computer-controlled diagonal-slit method of centering. From the systematic absences of ($h0l$, $l = 2n$) and ($0k0$, $k = 2n$) and subsequent least-squares refinements, the space group was determined to be $P2_1/c$. Data were collected at 295 K by using Mo Kα radiation and the ω–2θ scan technique on an Enraf-Nonius CAD-4 automated diffractometer. As a check on crystal and electronic stability, three representative reflections were measured every 120 min. The intensities of these standards remained essentially constant, within experimental error, throughout data collection, so no correction for decay was applied. The data were corrected for Lorentz and polarization effects, but not for absorption. Intensities of equivalent reflections were averaged. The agreement factor for the 341 averaged observed and accepted reflections was 1.4 on the basis of intensity and 1.1% on the basis of F_o. All calculations were performed on a VAX-11/750 computer using the SDP package of programs.[15] A summary of the crystal data, experimental details, and refinement results is listed in Table I, and atomic positional parameters are listed in Table II.

Table II. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B, $Å^2$
Cu1	0.15570 (6)	0.03832 (4)	0.09577 (7)	4.61 (1)
Cu2	0.34548 (6)	−0.05764 (4)	−0.03859 (7)	4.44 (1)
O1	0.0972 (4)	0.0573 (2)	0.2570 (4)	5.55 (9)
O2	0.4405 (3)	−0.1435 (2)	−0.0291 (4)	5.54 (9)
O3	0.2315 (3)	0.0207 (2)	−0.0526 (3)	4.29 (8)
N1	0.2527 (4)	−0.0409 (2)	0.2066 (4)	4.4 (1)
N2	0.3202 (4)	−0.0844 (2)	0.1460 (4)	4.6 (1)
N3	0.0439 (4)	0.1049 (3)	−0.0290 (5)	5.3 (1)
N4	0.3933 (4)	−0.0157 (3)	−0.1982 (4)	5.0 (1)
C1	0.0095 (5)	0.1008 (3)	0.2651 (5)	4.6 (1)
C2	−0.0204 (5)	0.1056 (3)	0.3958 (5)	5.3 (1)
C3	−0.1131 (6)	0.1488 (3)	0.4089 (6)	5.8 (1)
C4	−0.1799 (5)	0.1875 (3)	0.2931 (6)	5.9 (1)
C5	−0.1526 (5)	0.1854 (3)	0.1667 (6)	4.9 (1)
C6	−0.0573 (5)	0.1423 (3)	0.1473 (5)	4.4 (1)
C7	−0.0371 (5)	0.1423 (3)	0.0115 (6)	4.8 (1)
C8A	0.0303 (9)	0.1198 (7)	−0.1929 (9)	4.8 (2)
C8B	0.350 (1)	0.0545 (6)	−0.269 (1)	6.3 (3)
C9A	0.1552 (9)	0.1276 (6)	−0.2075 (9)	4.7 (2)
C9B	0.222 (1)	0.0611 (7)	−0.286 (1)	5.6 (3)
C10A	0.2130 (8)	0.0538 (6)	−0.1952 (8)	4.0 (2)
C10B	0.198 (1)	0.078 (1)	−0.147 (1)	7.3 (3)
C11A	0.335 (1)	0.0563 (7)	−0.234 (1)	7.8 (3)
C11B	0.067 (1)	0.1038 (8)	−0.160 (1)	6.6 (3)
C12	0.4712 (5)	−0.0428 (3)	−0.2549 (6)	5.2 (1)
C13	0.5346 (5)	−0.1105 (3)	−0.2082 (5)	5.0 (1)
C14	0.6253 (6)	−0.1279 (4)	−0.2769 (6)	6.8 (2)
C15	0.6957 (6)	−0.1888 (4)	−0.2334 (7)	7.5 (2)
C16	0.6729 (6)	−0.2355 (4)	−0.1330 (8)	7.7 (2)
C17	0.5849 (5)	−0.2219 (3)	−0.0663 (6)	6.3 (2)
C18	0.5163 (5)	−0.1565 (3)	−0.1015 (5)	4.9 (1)
C19	0.2647 (5)	−0.0657 (4)	0.3393 (6)	5.6 (1)
C20	0.3421 (5)	−0.1242 (3)	0.3677 (5)	5.7 (1)
C21	0.3725 (5)	−0.1349 (3)	0.2444 (5)	5.2 (1)

Structure Solution and Refinement. The structure was solved by using direct methods.[17] The copper, oxygen, and nitrogen atoms were located on an E map with probability statistics: absolute figure of merit = 1.16, residual = 5.42, and ψ_0 = 1.919. The remaining atoms were located by using successive difference Fourier syntheses. Hydrogen atoms were not located experimentally but were placed in calculated positions and added to the structure factor calculations.

The refinement based on an ordered arrangement of molecules converged with an agreement factor of 15.1%. A difference Fourier map showed peaks near C8, C9, C10, and C11, which corresponded to a reversal of the five- and six-membered chelate rings. These four atoms were subdivided into two groups, A and B, with each atom being assigned a multiplicity of 0.5. To obtain initial convergence, it was necessary at first to hold the temperature factors of these atoms isotropic. Eventually, it was possible to perform an anisotropic refinement of the disordered positions, beginning with a shift damping factor of 0.25 and later increasing to full shifts. Final convergence was obtained with all non-hydrogen atoms assigned variable anisotropic temperature factors. Hydrogens were included in calculated positions with estimated isotropic temperature factors and appropriate multiplicities.

The structure was refined by using full-matrix least-squares methods where the function minimized was $\sum[w(|F_o| - |F_c|)^2]$ and the weight w is defined as $4F_o^2/\sigma(F_o^2)$. Scattering factors were taken from Cromer and Waber,[18] and anomalous dispersion effects were included in F_c, with the values for f' and f'' obtained from Cromer.[19] The final cycle of

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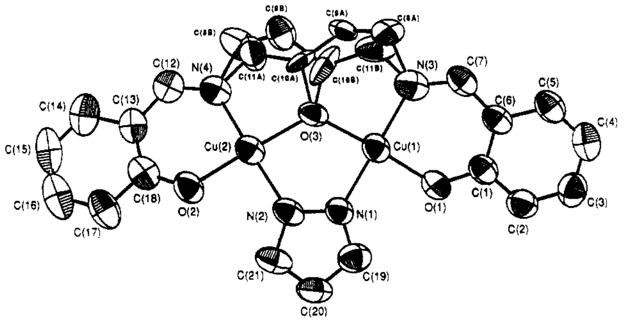

Figure 1. Structure and numbering scheme for **2** displaying 50% probability elipsoids.

Table III. Structural Parameters

atoms	1[a]	2	3[a]
	Distances (Å)		
Cu1-Cu2	3.349	3.360	3.401
Cu1-O1	1.892	1.900	1.911
Cu1-O3	1.918	1.914	1.942
Cu1-N1	1.953	1.960	1.947
Cu1-N3	1.945	1.946	1.940
Cu2-O2	1.847	1.902	1.903
Cu2-O3	1.918	1.932	1.961
Cu2-N2	1.946	1.950	1.923
Cu2-N4	1.933	1.937	1.934
	Angles (deg)		
Cu1-O3-Cu2	121.7	121.8	121.3
Cu1-N1-N2	120.0	120.6	122.8
Cu2-N2-N1	120.6	120.3	120.6
O3-Cu1-N3	82.6	90.8	95.4
O3-Cu1-O1	176.4	173.7	169.2
O3-Cu1-N1	88.6	88.1	86.7
N3-Cu1-O1	95.2	93.5	92.1
N3-Cu1-N1	163.7	171.4	175.6
O1-Cu1-N1	94.2	88.3	86.2
O3-Cu2-N4	82.6	90.3	91.8
O3-Cu2-O2	173.5	172.4	166.8
O3-Cu2-N2	88.4	88.3	88.0
N4-Cu2-O2	96.2	93.5	92.8
N4-Cu2-N2	166.2	167.8	164.9
O2-Cu-N2	93.8	89.3	90.8
Dihedral Angles (deg) (between Coordination Planes)			
	172.6	164.2	162.8

[a] Data taken from table of structural parameters in ref 10.

refinement included 307 variable parameters and converged with unweighted and weighted agreement factors of $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.054$ and $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2} = 0.072$. The highest peak in the final difference Fourier map had a height of 0.82 e/Å^3. Plots of $\sum(|F_o| - |F_c|)^2$ vs $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends. Tables containing structure factors, hydrogen coordinates, thermal parameters, torsion angles, and least-squares planes are available from R.M.B. upon request and have been deposited at the Cambridge Crystallographic Data Center.

Magnetic Susceptibility Studies. Variable-temperature, solid-state magnetic susceptibility data were obtained on a SQUID Series 800 VTS-50 susceptometer (SHE Corp.). A magnetic field strength of 10 kG was used during data aquisition. A diamagnetic correction was estimated from Pascal's constants[20] ($\chi_{dia} = -232.5 \times 10^{-6}$ cgsu) and used to correct experimental susceptibility data, yielding molar susceptibilities of the compound. These molar susceptibilities were fitted to the appropriate theoretical expressions by using a least-squares fitting program. The J value was determined by simulation of the experimental χ/T curve using $g = 2.145$, TIP = 120 × 10^{-6}, and IMP = 0.29%.

Determination of Orbital Projections. Projection of Cu atoms and donor atoms onto the best least-squares planes was accomplished by using a program developed by D.E.W. (Program No. GTP87) for use on a Chromatic CGC-7900 terminal. Values for α were determined according to the methods outlined by Nishida et al.[13]

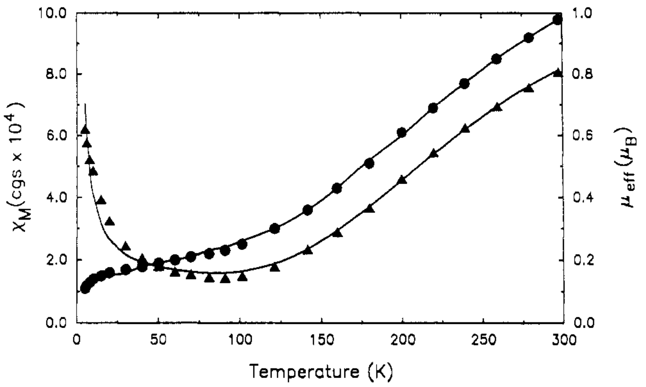

Figure 2. Plots of the molar paramagnetic susceptibility per molecule, χ_M, versus temperature and of the effective magnetic moment per molecule, μ_{eff}, versus temperature for **2**. The solid lines represent least-squares fitting of the data.

Table IV. Values for $-2J$ and Angle α Used in Overlap Integral Calculations

complex	$-2J$, cm^{-1}	α,[a] deg
1	310	3.6
2	540	0.6 ± 0.2 (av)
3	595	-0.6

[a] Value for α was determined by using the equation generated by Nishida et al.[10]

Results

Description of Crystal Structure. Compound **2** is essentially isostructural with the previously reported complexes, **1** and **3**. An ORTEP plot of **2** is shown in Figure 1. Atomic positional parameters and anisotropic thermal parameters for all non-hydrogen atoms are listed in Tables S3 and S4 (Supplementary Material), respectively. Selected bond distances and angles are listed in Table III. Complete listings of pertinent bond distances and angles have been included as supplementary material.

The two copper ions are bridged by an alkoxide oxygen and two pyrazolate nitrogen atoms. Overall, the complex is relatively planar, though a slight propeller twist is observed near the edge of the molecule centered around atoms C8 and C9. This twist is due to the presence of a six-membered chelate ring containing C8 and C9. The angle between coordination planes is 164.2°, comparable to angles of 172.6 and 162.8° observed for **1** and **3**, respectively. Since the backbone structure of **4** is asymmetric, two structural isomers are possible for **2**. The superposition of both forms is observed in the crystal structure of the complex. The structure was successfully solved by assigning each of the disordered backbone carbon atoms of the chelate rings 50% occupancy factors during refinement.

In the structure of **1**, no significant twisting of the molecular plane of the complex is observed, since the backbone structure of the complex contains two five-membered chelate rings. On the other hand, compound **3**, with two six-membered chelate rings, shows considerable twisting of the two coordination planes. Interestingly, there is no significant difference in the Cu–O–Cu angles of **1**–**3**, 121.7, 121.8, and 121.3°, respectively (cf. Table III). The Cu–O and Cu–N lengths of **2** are comparable with lengths reported for **1** and **3** and other alkoxide-bridged binuclear Cu(II) complexes.[9,10,14] The Cu–Cu separation in **2** is 3.360 Å. The intraligand bond distances and angles are normal, and the metal–ligand bond angles seem closer to values reported for compound **3**. The sum of the bond angles around the bridging oxygen atom is 359.6°, indicating that the bonds around this oxygen atom are essentially planar.

Magnetic Properties of 2. Magnetic susceptibility data of **2** were obtained between 297.5 and 5.0 K. A plot of the magnetic data as a function of temperature is shown in Figure 2. The room-temperature μ_{eff} value of 0.98 μ_B drops off gradually to 0.11

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μ_B at 5 K. The data were fitted by using the Bleaney–Bowers equation,[21] yielding $-2J = 545.6$ cm^{-1}, $g = 2.145$, and $N_\alpha = 120 \times 10^{-6}$ cgs emu. The exchange coupling parameter, $-2J$ (Table IV), is 310 and 595.6 cm^{-1} for **1** and **3**, respectively.[13] The value of $-2J$ for **2** indicates that the strength of the exchange interaction is between that of **1** and **3** and appears to be related to the distortions in the structure of the complex.

Discussion

Correlation of Structural and Magnetic Properties. In general, several structural features of binuclear copper(II) complexes are thought[4,5] to regulate the strength of exchange coupling interactions: (i) the dihedral angle between the two coordination planes, (ii) planarity of the bond around the bridging oxygen atom, and (iii) the Cu–O–Cu bridging angle. The dihedral angle between the two coordination planes is considered to be a key factor in determining the magnitude of the spin-exchange interaction. The larger the dihedral angle, the greater the strength of the exchange coupling. However, inclusion of six-membered chelate ring(s) in the structure of **2** and **3** causes distortions that decrease the dihedral angle. As shown in Table III, the dihedral angle decreases in the order **1** > **2** > **3**, while $-2J$ decreases (Table IV) in the opposite order **3** > **2** > **1**. This indicates that the dihedral angle of the coordination sphere of unsymmetric doubly bridged complexes may play only a minor role in determining the exchange interacion.

Planarity of the bonds about the bridging oxygen atom also has been cited as a factor influencing the nature of the spin-exchange interaction.[4] Curiously, for **2** the sum of the angles about the bridging oxygen is 359.6°, which is close to the idealized 360° angle expected for complete planarity. Again, this criterion by itself does not accurately predict the trend in $-2J$ values. Perhaps the most widely accepted criterion for correlating structure and magnetism is the Cu–O–Cu bridging angle.[4] This factor has been invaluable in systematically correlating the degree of interaction in both singly and doubly alkoxide- (or hydroxide-) bridged copper complexes.[5] Once, again, this factor fails to account for the variation in $-2J$ values in compounds **1**–**3**, since the Cu–O–Cu angles vary only between 121.3 and 121.8°, a variation too small to be considered significant and one that is not systematic (**2** < **1** < **3**).

Clearly, a different approach must be employed in order to correlate the structural and magnetic properties of **1**–**3**. Since the usual criteria employed to correlate magnetism in alkoxide-bridged binuclear copper complexes are not pertinent here, two principal questions remain to be answered. First, how does the pyrazolate ion influence the extent of magnetic exchange? Second, what is the mutual influence of the bridging ligands on $-2J$?

Very recently a binuclear copper complex was reported in which the metals are bridged by two pyrazolate ions and a chloride ion. The $-2J$ value for this complex is approximately 240 cm^{-1}.[22] These results suggest that bridging pyrazolate ions are capable of promoting antiferromagnetic exchange coupling. In addition, several examples of binuclear complexes, containing triazolate ion bridges, have been structurally characterized[23,24] and found to contain antiferromagnetically coupled metal centers.

Hoffmann and co-workers[11] have analyzed exchange interactions in bimetallic complexes in terms of pairwise interactions of molecular orbitals. In their equation

$$E_T - E_S = -2K_{ab} + \frac{2(\epsilon_1 - \epsilon_2)^2}{J_{aa} - J_{ab}} \qquad (1)$$

the quantity $(\epsilon_1 - \epsilon_2)$ is the important term. Since compounds **1**–**3** are so closely related structurally and distortions are relatively minor, the denominator in (1) would be expected to vary slowly. Similarly, K_{ab} is usually only on the order of a few reciprocal centimeters[11] and would be expected to be nearly constant in the series **1**–**3**, so the expression for $-2J$ in (1) is commonly dominated by the second term.

The quantities ϵ_1 and ϵ_2 represent the energies of molecular orbitals obtained from the interaction of metal d magnetic orbitals with atomic and molecular orbitals residing on the bridging ligands. For the series **1**–**3**, atomic orbitals on the alkoxide and HOMO's on pyrazolate ions are considered combined with magnetic $d_{x^2-y^2}$ orbitals on the metal centers, producing new molecular orbitals, designated d_a'' and d_s'', with energies ϵ_1 and ϵ_2. According to Hoffmann et al.,[11] the square of the difference in energy between these two new orbitals largely determines the magnitude of the $-2J$ value. By symmetry, a given bridging ligand orbital will generally interact with one combination of magnetic orbitals, whether symmetric (d_s) or antisymmetric (d_a) in preference to the other combination. If the bridging ligands work to stabilize the same combination of magnetic orbitals, then the former are said to work in a complementary fashion, and the antiferromagnetic exchange interaction is enhanced. Conversely, bridging ligands that attempt to stabilize different combinations of magnetic orbitals are said to work in a countercomplementary fashion, which tends to attenuate antiferromagnetic exchange interactions.

Recently, Nishida et al.[13] have utilized a semiquantitative correlation of magnetostructural properties of **1** and **3** to show that $-2J$ for **1** would be expected to be less than that of **3**. Such a trend is indeed observed experimentally. Their approach involves calculation of the HOMO's on the pyrazolate ion and an analysis of the interaction between magnetic d orbitals and ligand HOMO's to produce d_a'' and d_s''. As with all molecular orbitals, the energies of d_a'' and d_s'' depend on the energies of the interacting orbitals and the overlap integrals between the interacting orbitals. Nishida calculated ligand HOMO's, ψ_a and ψ_s, which interact with the copper magnetic orbitals, yielding $E_{\psi s}$ and $E_{\psi a}$, separated in energy by 0.17 eV. They concluded from their analysis that the orbital energies of the pyrazolate bridge are acting in a complementary fashion with the alkoxide bridge to enhance the antiferromagnetic exchange interaction. However, this is inconsistent with the notion that an alkoxide bridge with an obtuse Cu–O–Cu angle provides better overlap with d_a, the antisymmetric combination of magnetic orbitals. In their study, Nishida et al. show that when ψ_s is higher in energy than ψ_a (empirically this is observed), the splitting between d_a'' and d_s'' from an energy standpoint is actually *compressed*. The energies of the interacting orbitals appear to cause the pyrazolate bridge to work in a countercomplementary fashion with the alkoxide bridge. However, if ψ_a overlaps more effectively with d_a than ψ_s with d_s, the overlap integrals between interacting orbitals favor enhancement of antiferromagnetic exchange coupling. In other words, overlap considerations may influence the pyrazolate bridge to act in a complementary fashion with the alkoxide bridge to increase $-2J$.

In Nishida's study, the pertinent overlap integrals are expressed as $S(d_s,\psi_s)$ and $S(d_a,\psi_a)$ and are given as functions of α,[13] the angle between the Cu–(pyrazolate N) bond vector and the nearest lobe of the local magnetic d orbital. They determined approximate values for $S(d_s,\psi_s)$ and $S(d_a,\psi_a)$ and evaluated the difference $S(\text{a–s}) = S(d_a,\psi_a) - S(d_s,\psi_s)$ for both **1** and **3** (Table III). The value of $S(\text{a–s})$ for **3** was found to be larger than the value for **1**. Actually, $-2J$ for **3** is close to the value reported for a single-alkoxide-bridged binuclear copper complex studied previously by Nishida[6] where $-2J = 635$ cm^{-1} and the Cu–O–Cu angle was 137.7°, representing an ideal if not limiting case of exchange through an alkoxide bridge. Evidently, the energies of the interacting orbitals and overlap integrals nearly offset each other in **3** so that in effect the pyrazolate bridge contributes little to the antiferromagnetic exchange interaction. On the other hand, in **1** the pyrazolate bridge appears to function in a countercomplementary fashion with the alkoxide ion.

A natural question arises from the discussion above as to the magnitude of $-2J$ for **2**. It is perhaps not surprising that this value is intermediate between those for **1** and **3**, since the structural variations responsible for the change in $-2J$ are systematic in going from **1** to **3**. However, how is it that $-2J$ for **2** is much closer to

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that for **3**? The unsymmetrical nature of the ligand backbone in **2** lowers the symmetry of the complex from the C_{2v} observed in the other structure. This means that the angle α is slightly different for each copper center. Projecting the Cu and donor atoms on a plane, in a manner similar to that used by Nishida et al.,[13] we have evaluated α for **2**. An average value of α (0.6 ± 0.2°) used (see Table IV) in our calculations is much closer to the value reported for **3** and gives a value of S(a–s) that correlates very well with $-2J$ (supplementary material).

Even though the overlap integrals evaluated by using data from Jaffe[25] and Kuroda[26] are rough, the fact that α and S(a–s) are quite similar for **2** and **3** appears to correlate nicely with the fact that $-2J$ for **2** and **3** are also quite close. These data suggest that the pyrazolate bridge exerts conflicting influences on the magnetic exchange in the systems. On the one hand, the energy spacing of the pyrazaolate HOMO's indicates that pyrazolate and alkoxide function in a countercomplementary fashion with respect to the exchange process. On the other hand, since the antisymmetric MO's overlap is more effective (note S(a–s) is positive for **1–3**), this overlap factor competes with the energy factor causing the pyrazolate to act in a complementary fashion with respect to the alkoxide ion. Although the precise contribution of each of the bridging species to the magnitude of the exchange interaction was not determined in this work, it appears that an unfavorable energy factor that attenuates magnetic exchange is increasingly offset by a favorable overlap factor in complexes **1–3**.

Summary

A new pyrazolate-bridged binuclear copper(II) complex (**2**) has been synthesized with the asymmetric ligand **4**. The crystal structure of **2** is isostructural with that of **1** and **3**. The magnetic properties of **2** have been evaluated and compared with results reported previously for **1** and **3**. The pyrazolate bridge in **2** appears to participate in a complementary fashion with the alkoxide bridge to enhance the strength of the antiferromagnetic exchange interaction.

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Supplementary Material Available: Tables containing a complete listing of bond lengths and bond angles, positional parameters for hydrogens and their esd's, anisotropic thermal parameters for all non-hydrogen atoms, torsion angles, least-squares planes, and magnetic data and a figure showing the correlation of $-2J$ and S(a–s) for compounds **1–3** (16 pages); a listing of F_o and F_c (10 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of a Technetium(III) Nitrosyl Compound: $Tc(NO)(Cl)(SC_{10}H_{13})_3$

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Upon the reaction of $(n\text{-Bu}_4N)[Tc(NO)Cl_4]$ with 2,3,5,6-tetramethylbenzenethiol, the neutral compound $Tc(NO)(Cl)(tmbt)_3$ is obtained. The infrared spectrum shows a band at 1798 cm^{-1} from the linear nitrosyl group, establishing the metal oxidation state of +3. ^1H NMR data indicate that this diamagnetic compound is analogous to a series of trigonal-bipyramidal, 14-electron compounds in which the thiolate ligands are bound in the equatorial plane and the remaining two ligands sit in the axial sites. The X-ray crystal structure of $Tc(NO)Cl(tmbt)_3$ confirms this ligand disposition with the thiolates adopting the "two-up-one-down" conformation. Crystal data for $C_{30}H_{39}NOS_3ClTc$: monoclinic space group $C2/c$, $a = 24.420$ (5) Å, $b = 14.701$ (4) Å, $c = 17.500$ (4) Å, $\beta = 93.50$ (2)°, $V = 6271$ (5) $Å^3$ to give $Z = 8$ for $D_{calc} = 1.394$ g/cm^3; structure solution based on 7457 reflections converged at $R = 0.056$, $R_w = 0.067$.

Introduction

Although the preparation of the first technetium nitrosyl compound was reported in 1963,[1] it was only identified as such 12 years later[2] and, even now, few technetium nitrosyl compounds are known. The isolation of $[Tc(NO)Br_4]^-$ has been reported,[3] as well as a limited number of Tc(I) and Tc(II) complexes with nitrosyl groups and various coligands.[4-6] Recently, Thornback et al. published a convenient, high-yield synthesis of $(n\text{-Bu}_4N)[Tc(NO)Cl_4]$,[7] which has prompted renewed interest in the technetium nitrosyl core.

We have shown elsewhere[8] the tendency of the ligand 2,3,5,6-tetramethylbenzenethiolate (tmbt) to stabilize technetium(III) complexes. The planar thiolate core $Tc(tmbt)_3$ binds two of a number of different π-accepting ligands (MeCN, *i*-PrNC, CO, py, PEt_3) to form five-coordinate, trigonal-bipyramidal compounds. The incorporation of the NO^+ group as a π-accepting ligand into such Tc(III) centers is described herein.

Experimental Section

Caution! Technetium-99 is a weak β^- emitter ($E = 0.292$ MeV, $t_{1/2} = 2.12 \times 10^5$ years). All work has been done in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsewhere.[9]

Ammonium pertechnetate was supplied as a gift by Du Pont/Biomedical Products. Reagents and solvents were used as received unless otherwise indicated. The nitrosyl complex $(n\text{-Bu}_4N)[Tc(NO)Cl_4]$ was

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