398 *Inorg. Chem.* **1986**, *25*, 398-400

between the charged ligand and the metal ion. Figure 2 shows a plot of Δ log *K* values vs. charge density (e/d^3 where e = charge, d = diameter). Indeed, the change in log *K* (Δ log *K*) in going from the neutral to the deprotonated form is proportional to the charge density; i.e., the larger the charge density, the greater the change. The net result of this effect is the complete reversal of the formation constant ordering, i.e. $Ca^{2+} \geq Na^+ > K^+$. This result is consistent with the competitive extraction data for Na^+ and K^+ originally reported by Bartsch et al.

In summary, we have demonstrated that by attaching an ionizable pendent group to a crown ether, the ligand selectivity toward metal ion binding can be tuned by simply adjusting the pH of the medium. This mechanism may be very important in biological ion transport through membranes with ionizable ionophores such as monensin and nigericin.

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Contribution from the Department of Chemistry, University of Florence, and ISSECC, CNR, Florence, Italy

Magnetic Coupling in a Linear-Chain Copper(II)-Imidazolate Compound. Mechanism of the Exchange Interaction through Bridging Imidazolate Ligands

A. Bencini,[1a] C. Benelli,[1b] D. Gatteschi,*[1b] and C. Zanchini[1b]

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The crystal structure of *catena*-(μ-imidazolato)chlorobis(imidazole)copper(II), $CuCl(iz)(izH)_2$, was reported some years ago,[2] and the compound was found to contain linear chains of imidazolato-bridged copper(II) complexes. In view of the current interest in the characterization of the magnetic properties of one-dimensional magnetic materials[3] and of the mechanism of the exchange interaction between transition-metal ions transmitted by imidazolate and similar bridges,[4-8] we decided to measure the temperature dependence of the magnetic susceptibility of $CuCl(iz)(izH)_2$, and we wish to report here the results of such an analysis, together with an interpretation of the mechanism of exchange on the basis of an extended Hückel treatment.

Experimental Section

catena-(μ-Imidazolato)chlorobis(imidazole)copper(II) was prepared according to the reported procedure. The magnetic susceptibility was measured with a Faraday balance, equipped with a Bruker electromagnet, and a R-100 Cahn microbalance. A CF 200 flow cryostat from Oxford Instruments was used to regulate the temperature. EPR spectra were recorded with a Bruker ER 200 spectrometer.

Extended Hückel calculations were performed with a locally generated program. Standard parameters[9] were used for the Cu, N, C, Cl, and H atoms.

Results and Discussion

The temperature dependence of the magnetic susceptibility of $CuCl(iz)(izH)_2$ in the range 10–300 K is shown in Figure 1. The magnetic susceptibility increases with decreasing temperature down to about 80 K, and below this it decreases, the compound becoming practically diamagnetic below 10 K.

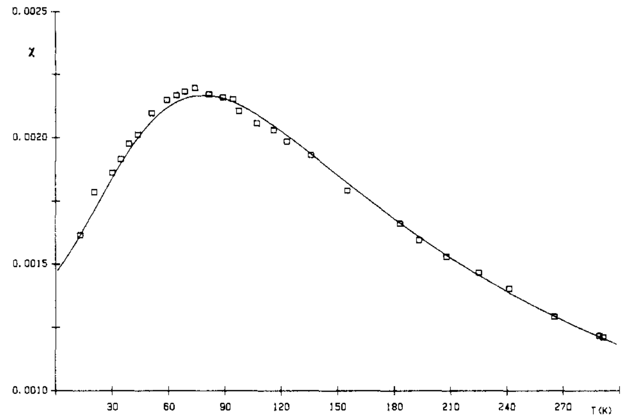

Figure 1. Temperature dependence of the magnetic susceptibility of $CuCl(iz)(izH)_2$ in the 10–300 K range. □ are the experimental points; the curve is calculated with best fit parameters through the Bonner–Fisher model for an $S = {}^1/_2$ antiferromagnetic chain.

Table I. Magnetic and Structural Parameters for Imidazolate-Bridged Copper(II) Complexes

	J, cm^{-1}	$\alpha_1{}^a$	$\theta_1{}^a$	$\alpha_2{}^a$	$\theta_2{}^a$	ref
$Cu_2bpim^{3+\,c}$	163	176.2	4.7	171.1	13.4	11
$Cu_3(iz)_2(izH)_8(ClO_4)_4$	117	162.9	70.0	160.9	60.0	6, 12
$CuCl(iz)(izH)_2$	84	169.4	90.0	168.8	90.0	2, *b*
$Cu_2(TMDT)_2(iz)(ClO_4)_2{}^{+\,d}$	52	161.9	91.8	160.2	90.0	4
$Cu_2(iz)(macro)^{2+\,e}$	42	158.9	68.8	166.3	79.1	13
$Cu_2(Gly\text{–}GlyO)_2(iz)^{-\,f}$	38	157.5	5.8	157.2	10.4	14

[a] The subscripts 1 and 2 refer to the two different metal ions bridged by the imidazolate and are defined in the text. [b] This work. [c] bpim = 4,5-bis[2-(((2-pyridyl)ethyl)imino)ethyl]imidazolate. [d] TMDT = 1,1,7,7-tetramethyldiethylenetriamine. [e] macro = the 30-membered "N_6O_4" macrocyclic Schiff base prepared from 2,6-diacetylpyridine and 3,6-dioxaoctane-1,8-diamine. [f] Gly–GlyO = glycylglycinate.

Since the structure indicates a linear chain, the experimental points, in the range 10–300 K, were fit with a Bonner–Fisher treatment,[10] yielding $g = 2.182$ (1) and $J = 84.2$ (1) cm^{-1}. Note that we use the Heisenberg spin Hamitonian in the form: $H = J\mathbf{S}_1\cdot\mathbf{S}_2$, a positive J value corresponding to an antiferromagnetic interaction. Below 10 K the magnetic behavior deviates from that expected for a Heisenberg linear chain, indicating that higher order interactions occur. The agreement of the calculated curve with the experimental points can be considered as good, thus confirming the essentially linear magnetic chain behavior of the compound.

The polycrystalline powder EPR spectra of $CuCl(iz)(izH)_2$ recorded at room temperature are fairly broad, with a *quasi* isotropic signal centered at $g = 2.10$. No sharpening is observed on cooling down the sample: the lines remain broad to the point where they disappear due to the antiferromagnetic coupling.

The extent of the coupling is fairly large in $CuCl(iz)(izH)_2$, the second largest thus far reported for copper(II) complexes bridged by imidazolate ligands,[4,6] while a much higher coupling was observed in a case in which the imidazolate moiety is a part of a chelate ligand[4] (see Table I).

The mechanism of the exchange interaction transmitted by a bridging imidazolate has been discussed several times,[4-6] on the basis of qualitative considerations, taking into account the nature

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(1) (a) ISSECC, CNR. (b) University of Florence.

(2) Lundberg, B. K. S. *Acta Chem. Scand.* **1972**, *26*, 3902.

(3) "Magneto-Structural Correlations in Exchange Coupled Systems"; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; Reidel: Dordrecht, 1985.

(4) Kolks, G.; Lippard, S. J.; Waszczak, J. V.; Lilienthal, H. R. *J. Am. Chem. Soc.* **1982**, *104*, 717.

(5) Felthouse, T. R.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 2636.

(6) Benelli, C.; Bunting, R. K.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1984**, *23*, 3074.

(7) van der Griendt, B.; Hasnoot, J. G.; Reedijk, J.; de Jongh, L. J. *Chem. Phys. Lett.* **1984**, *111*, 161.

(8) Drew, M. G. B.; Nelson, S. M.; Reedijk, J. *Inorg. Chim. Acta* **1982**, *64*, L189.

(9) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.

(10) Bonner, J. C.; Fisher, M. E. *Phys. Rev.* [*Sect.*] *A* **1964**, *135*, 640.

(11) Dewan, J. C.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 2079.

(12) Ivarsson, G.; Lundberg, B. K. S.; Ingri, N. *Acta Chem. Scand.* **1972**, *26*, 3005.

(13) Drew, M. G. B.; McCann, M.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1868.

(14) Matsumoto, K.; Ooi, S.; Nakao, Y.; Mori, W.; Nakahara, A. *J. Chem. Soc., Dalton Trans.* **1981**, 2045.

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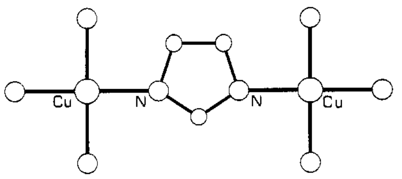
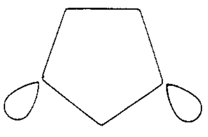


Figure 2. Structure of the model complex used in MO calculations. The terminal ions can be either Cl^- or NH_2^-.

of the interacting metal and ligand orbitals. In general, there is agreement that the π orbitals of the imidazolate ligand are not involved in the coupling.[4-6] As a consequence of this assumption, it is expected that in a series of copper complexes where the magnetic orbital on the metal ion can be described as $x^2 - y^2$, the extent of the antiferromagnetic coupling must depend on the Cu–N–N angle, α, the N's being the nitrogen atoms of the imidazolate ligand. The coupling should be antiferromagnetic for $\alpha = 180°$ and decrease with decreasing α, but this prediction has hardly found confirmation in the experiment, as one can see from Table I. It was also suggested that J might depend on the pK_a of the bridging ligand,[4] but the large differences observed in three different complexes with the identical imidazolate bridge[4,6] have definitely eliminated this possibility. Finally, another angle was also taken into account, namely θ, the dihedral angle between the plane of the magnetic orbital on the copper(II) ions and the imidazolate plane. However, it was anticipated that the role of this angle might become important only for exchange interactions between the two copper ions and this should not be the case when the magnetic orbital is essentially $x^2 - y^2$, i.e. antibonding.

Since this compound seems to add a contribution to the confusion, because α is closer[2] to 180° than in $Cu_3(iz)_2(iz)_8(ClO_4)_4$ while it has a smaller antiferromagnetic coupling, we attempted to have a semiquantitative estimate of the factors affecting the extent of coupling through imidazolato bridges by using extended Hückel calculations on model dimeric units according to the model suggested by Hoffmann et al.[9] The model compounds we studied are $[Cu(NH_2)_3(iz)Cu(NH_2)_3]^{3-}$ and $[CuCl_3(iz)CuCl_3]^{3-}$ with the geometry shown in Figure 2.

The electronic structure of the dinuclear units has been analyzed with the fragment MO method[15] using $(CuX_3)_2^{2-}$ ($X = Cl^-, NH_2^-$) and iz^- moieties. The relative energies of the HOMO's of $(CuX_3)_2^{2-}$ and the highest occupied MO's of iz^- are shown in Figure 3, together with the energies of the MO's of the whole molecule. This analysis shows that the symmetric combination of the fragment metal orbitals, which are essentially $x^2 - y^2$, overlaps with a MO of iz^- that has large contributions from the nitrogen orbitals and that can be described as shown in **1**, with the main lobes substantially bent from the N–N direction. The antisymmetric combination, on the other hand, involves a ligand orbital that has a slightly lower energy, with the lobes essentially parallel to the N–N direction, as shown in **2**. Since the energy difference between the ligand orbitals in **1** and **2** is fairly small (0.041 eV), the energies of the symmetric (S) and antisymmetric (A) dimer molecule orbitals are largely overlap-determined. The energy difference between S and A, which according to Hoffman's model[9] is related to the extent of antiferromagnetic coupling between the two copper ions, is strongly affected by the angle α, as shown in Figure 4. Indeed for $\alpha = 180°$ the antisymmetric combination is higher in energy as a consequence of the larger overlap of the metal magnetic orbitals with the ligand orbitals that are almost exactly directed along the lobes of the $x^2 - y^2$ orbitals. As the angle is varied, the overlap of the antisymmetric combination decreases and the corresponding energy decreases, while the overlap of the symmetric combination increases and the corresponding energy increases. At some angle, the two molecular orbitals must cross: with our set of parameters this occurs at $\alpha = 158°$. The prediction resulting from these calculations is that the extent of the antiferromagnetic coupling should decrease on decreasing α in the range 180–158°, ferromagnetic coupling should occur in proximity of $\alpha = 158°$, and again antiferromagnetic coupling should occur for $\alpha < 158°$.



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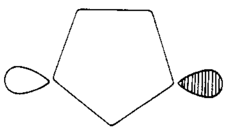

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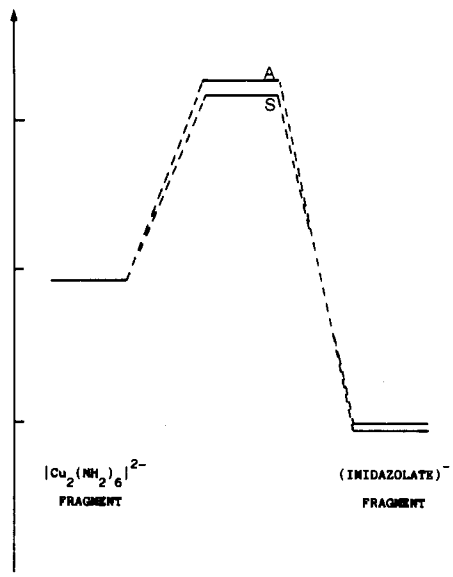

Figure 3. Relative energies (eV) of the HOMO's for $[Cu_2(NH_2)_6]^{2-}$ and imidazolate fragments, together with the energies of the relative MO's of the whole molecule.

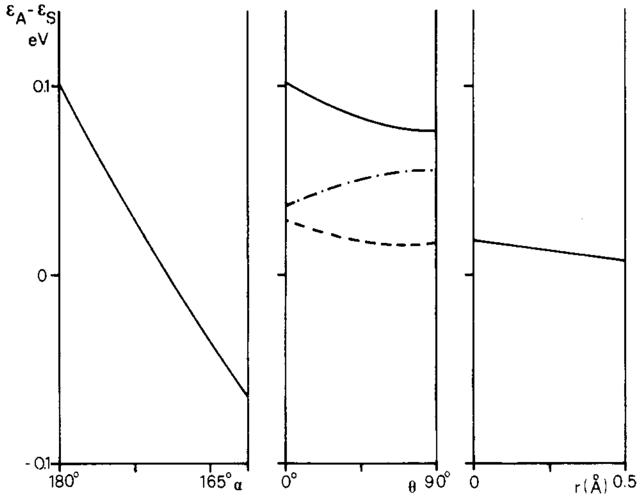

Figure 4. Variations of the energy difference, $\epsilon_A - \epsilon_S$, between the antisymmetric and symmetric combinations on changing (from left to right) the following: (a) α angle; (b) θ angle for $\alpha = 180°$ (—), $\alpha = 165°$ (---), and $\alpha = 150°$ (-•-); (c) elevation (r) of the copper(II) ion with respect to the four-N-donor plane.

The calculations show that also the other angle, θ, has indeed some effect on the energy differences between the two highest occupied MO's, as shown in Figure 4, and this is at first sight surprising, due to the σ nature of the ligand orbitals. However, the analysis of the fragments shows that the overlap of $[Cu(NH_2)_3]^-$ and iz^- is affected by the θ angle, and similar results are calculated also for $CuCl_3^-$. This variation is not due to the metal–imidazolate overlap but to that of the orbitals of the other atoms in the coordination sphere of copper and the imidazolate ligand. The effect is more marked for the antisymmetric than for the symmetric combination, and it tends to decrease the energy difference between S and A on increasing θ for $\alpha > 158°$, while

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(15) Hoffman, R.; Fujimoto, J. R.; Swenson, C.; Wan, C. C. *J. Am. Chem. Soc.* **1973**, *95*, 7644.

it has a reverse effect for $\alpha < 158°$. This result is clarifying in the sense that it explains why attempts to correlate J to the one parameter α have failed. Further, since the J dependence on θ is determined by ligand–ligand interactions, a too strict dependence of the experimental coupling on structural parameters cannot be obtained, because in principle all the copper coordination environment should be taken into account and not only the bridging ligand.

Finally, we took into consideration the deviation of the copper ion from the plane of the four nitrogen ligands, as it can occur in a square-pyramidal complex. The calculations, whose results are shown in Figure 4, were performed for $\alpha = 165°$ and $\theta = 0°$, showing that the energy difference decreases on moving copper out of the plane of the nitrogen donors, thus determining a smaller antiferromagnetic coupling.

From the above results, a rationalization of the data of Table I can be attempted. Cu_2bpim^{3+} is concurrently indicated by the large α and the small θ as the compound where the antiferromagnetic coupling must be the largest,[10] and indeed this is experimentally verified. The second largest d value was reported[6] for $Cu_3(iz)_2(izH)_8(ClO_4)_4$, but the second largest J is observed for $CuCl(iz)(izH)_2$. The explanation we can provide for this is that the latter has a larger[2,12] θ (90° vs. an average of 65°) and, perhaps most important, the copper ion is not square planar as in $Cu_3(iz)_2(izH)_8(ClO_4)_4$, but square pyramidal, deviating by 0.38 Å from the plane of the nitrogen donors.[2] Similar considerations hold also[4] for $Cu_2(TMDT)_2(iz)(ClO_4)_2^+$. The compound $Cu_2(iz)(macro)^{2+}$ is more difficult to discuss, since in this case the bridge is markedly asymmetric.[13]

Concluding Remarks

The extended Hückel analysis of the mechanism of the exchange interaction between two copper ions bridged by imidazolate ligands has shown that it is determined by the molecular orbitals of the ligand. The extent of the coupling depends essentially on two structural parameters, α and θ, the latter involving ligand–ligand rather than metal–ligand interactions. Although this makes structural–magnetic correlations difficult, some trend begins to appear to justify the experimental data.

Registry No. $CuCl(iz)(izH)_2$, 41619-57-2.

Additions and Corrections

1985, Volume 24

Seshadri Jagannathan and Ramesh C. Patel*: Kinetics of Electron Transfer from Tris(picolinato)chromate(II) to Iron(III).

Page 3634. In the abstract, last line, "k(formation) = 14.1 $M^{-1}\ s^{-1}$" should read "k(formation) = $2.15 \times 10^2\ M^{-1}\ s^{-1}$".

Page 3639. In Table VII, "k_{obsd}, min^{-1}" should read "k_{obsd}, h^{-1}".—Ramesh C. Patel