Electronic and Geometrical Structure of the Pyrazole Ligand co-ordinated to Metal Centres *

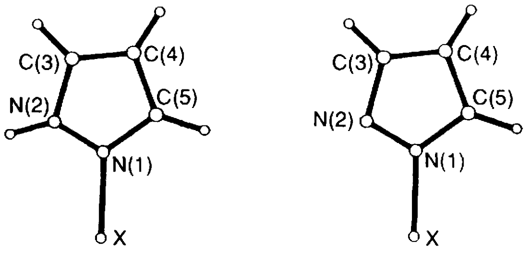
Piercarlo Fantucci[a] **and Venanzio Valenti**[b]
[a] *Department of Inorganic and Organometallic Chemistry, University of Milan, CNR Centre, Via Venezian 21, I 20133 Milano, Italy*
[b] *Department of Chemistry, University of Camerino, Via S. Agostino 1, I 62032 Camerino, Italy*

The electronic and geometrical structure of pyrazole (Hpz) and pyrazolate (pz) ligands co-ordinated to metal centres such as Na^+, Cu^+, CuF and $Cu(NH_3)^+$ or perturbed by a positive point charge has been investigated by means of *ab initio*, all-electron Hartree–Fock calculations. Extensive geometry optimization of the internal coordinates of Hpz and pz^- shows that the structure of the ligand is little affected by the presence of chemically different co-ordination centres, thus confirming the pronounced rigidity of the pyrazole ring. The co-ordination process appears to influence only the valence angles external to the ring; their values correlate well with the characteristics of the molecular orbitals localized on bonds involving the nitrogen donor atom. An analysis of the localized molecular orbitals has led to conclusions in agreement with the valence shell electron pair repulsion approach and Bent's rule.

The structural modifications undergone by ligands co-ordinated to a transition-metal atom (or perturbed by a Lewis-acid centre) are of primary importance in formulating qualitative theories of the co-ordination bond. In the case of ligands with an essential σ-donor character the distortions are expected to originate from variations in the spatial distribution of the electron pair on the donor atoms. Correspondingly, mainly the σ bonds are expected to be substantially modified. Ligands possessing π bonds and vacant π molecular orbitals (MOs) (*e.g.* CO, C_2H_4, O_2, *etc*) may be perturbed to a larger extent in the event that both σ and π mechanisms are operative. In some cases the changes in ligand geometries are so pronounced that they can be assumed as a proof of a specific bonding interaction and specific co-ordination geometry.

In general, however, ligand-geometry modifications cannot be interpreted on the basis of clearly separable σ and π contributions. Furthermore, it is difficult to make predictions and correlations between observed (or not observed) ligand-geometry variations and the extent of electronic rearrangements consequent upon the formation of a co-ordination bond. An interesting example for a discussion of all these aspects is the pyrazole (Hpz) ligand which shows good co-ordination properties both as a neutral and an anionic ligand. As a neutral ligand it undergoes protonation, or metallation, leading to H_2pz^+ and X(Hpz) species, while its anion leads to the formation of a variety of complex salts (see Fig. 1). Both Hpz and pz^- are usually considered as essentially σ donors, *via* the electron pair located on the N(1) atom, *i.e.* it is assumed that the pseudo-aromatic sextet does not take part in the metal–ligand bond.

Although the co-ordination and electronic situations involving pyrazole-like ligands are many and varied, it is known that the molecular structure of such ligands is almost unaffected by co-ordination. In the past the analysis of X-ray structural data led to the conclusion that Hpz and pz^- are characterized by a highly rigid structure, also from an electronic point of view, and that the perturbation acting on the lone pair on the N(1) atom is not sufficient to produce significant geometrical changes.[1,2] Recently Bonati[3] approached the problem of a more quantitative estimate of the ligand structure modifications in co-ordinated pyrazoles by means of a critical screening of the most accurate experimental data. Theoretical investigations on the relation between geometrical and electronic factors in Hpz or pz^- metal adducts have never been previously reported.



(*a*) (*b*)

Fig. 1 Atom numbering for (*a*) pyrazole adducts (X = CuF, Cu^+, Na^+ or point charge) and (*b*) pyrazolate salts [X = Na^+, Cu^+ or $Cu(NH_3)^+$]

This paper presents results of *ab initio* Hartree–Fock (HF) calculations carried out on a series of pyrazole adducts of type X(Hpz) (X = CuF, Cu^+, Na^+ or a point positive charge Q^+) and pyrazolate complexes like X(pz) [X = Cu^+, Na^+ or $Cu(NH_3)^+$]. Our aim is to show that the rules concerning the trend in structural properties, formulated by Bonati[3] on the basis of experimental data, can also be formulated by considering geometrical data obtained in a purely theoretical way.

The relevant geometrical parameters have been derived from an almost full geometry optimization. Thus the results obtained are intrinsically consistent because the level of accuracy is the same for all the considered systems. This is a prerequisite for a meaningful comparison of theoretical and experimental data.

A detailed discussion of the charge distribution will be presented to show if (and to what extent) the co-ordination bond causes electronic redistribution. Finally, the relations between the specific values of the internal coordinates of Hpz and pz^-, bound to a metal centre, and the spatial position of the centroids of the localized MOs (LMOs), in which the contribution of the N(1) donor atom predominates, will be shown. This leads to the interpretation of some features of the geometrical structure around the co-ordination centre, in terms

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* *Non-SI unit employed:* D $\approx 3.33 \times 10^{-30}$ C m.

of a rigorous, non-empirical, valence shell electron-pair repulsion (VSEPR)-like[4] approach.

Computational Method

The electronic and geometrical structure of pyrazole, considered both as a free molecule and as a neutral or anionic ligand interacting with metal centres, has been theoretically investigated by means of *ab initio* calculations, using the Hartree–Fock (HF) method and considering all the electrons. An assessment of the influence of the adopted basis set on the computed optimum geometry and electron distribution was performed for the free pyrazole molecule, using a small basis of Slater type orbital (STO)-3G type (basis A),[5] a split-valence STO 3-12G basis (basis B),[5] and a triple-zeta basis for valence orbitals, (6211/411) for N and C atoms and (311) for H atoms[6,7] (basis C).

Since basis B gave results for pyrazole (see next section) in fairly good agreement with the experiment, and heavy computational costs are not required, this was also adopted for H, C, N, F and Na atoms in the pyrazole adducts. For copper derivatives the basis set MIDI4[8] for Cu was adopted: the outermost functions were split into two components to give a double-zeta representation of the 4s and 3d orbitals (43321/43/31).

The energy results of these atomic basis sets are severely affected by basis-set superposition errors, thus preventing an accurate estimation of the absolute value of the stability of the metal adducts. However, this is beyond the scope of the present study.

The geometry optimization, carried out using analytical gradient techniques,[9] involves almost all the independent internal coordinates of the different systems studied. Only the following constraints have been imposed: (*i*) the pyrazole moiety is always considered as planar; (*ii*) the geometry of the NH_3 ligand in $Cu(NH_3)(pz)$ is taken from experiment[10] (N–H 1.016 Å, H–N–H 107.4°); (*iii*) a fixed value of 2.0 Å is assigned to the $Cu-N(NH_3)$ distance, which is close to the experimental one found in $[Cu(NH_3)_4]SO_4 \cdot H_2O$ (2.05 Å);[11] (*iv*) the X–Cu–N(pz) geometry (X = NH_3 or F) in $Cu(NH)_3(pz)$ and (CuF)(Hpz) is always assumed as linear; and (*v*) a value of 120° has been assigned to the X–N(1)–N(2) angle (X = positive point charge Q^+, Cu or Na) and kept constant in all the calculations on the adducts. This choice is based on the observation that the angle H–N(2)–N(1) (see Fig. 1) optimized for H_2pz^+ has a value of 121.5° (see Table 2).

The constraints imposed are expected to have little influence on the geometry around the atoms directly involved in the co-ordination, and are irrelevant to the structure of the pyrazole ligand itself since the internal coordinates of Hpz and pz^- have been fully optimized.

The search for minimum points on the molecular energy surface was considered as converged when all the components of the energy gradient were smaller than about 0.0005 au $bohr^{-1}$ or 0.0005 au rad (au = 27.21 eV = 2625.5 kJ mol^{-1}, bohr = 5.21977×10^{-11} m). This guarantees a numerical accuracy better than 0.003 Å for bond distances and 0.03° for valence angles. Since the numerical accuracy of the theoretical values is higher than the accuracy of the experimental data, especially when obtained from X-ray diffraction, the comparison between theory and experiment is not affected by numerical inconsistencies.

The electron distribution was analysed according to the conventional Mulliken method. This procedure has been subject, even recently, to strong criticisms (see, for instance, ref. 12), especially when applied to transition-metal compounds. However we believe that under well controlled conditions the Mulliken analysis is a valuable tool for interpreting the electron distribution. In fact, in the past, concepts of basic importance in co-ordination chemistry, like donor–acceptor properties and the extent of bonding and back-bonding charge transfer, have been derived just with the help of Mulliken analysis. It is often stated that the Mulliken partitioning of the electronic charge cannot be applied to molecular systems in which very diffuse basis functions (or atomic orbitals) are included. This could occur in the case of the outermost s and p orbitals of the transition-metal atoms: the overlap charge assigned to the metal is actually located in regions nearer to the ligand centres. However, the present study is free from these shortcomings for the following reasons: first the MIDI4 basis adopted for the copper atom does not include very diffuse functions; secondly, since the net atomic charge on the copper atom is always positive and relatively high (0.6–0.7) (a fact which agrees with chemical expectation), the 4s and 4p orbitals are characterized by definitely small occupancies. The small contribution of the most diffuse orbitals to the total wavefunction validates the Mulliken analysis. Thirdly, the following discussion will be based mostly on relative variations of electron populations and not on their absolute values.

The charge distribution analysis was also carried out for LMOs with the aim of interpreting geometrical features of the bonds involving the nitrogen donor atom in terms of the interaction between the associated electron pairs. The relation of such an analysis to the VSEPR[4] approach is evident. The LMOs were determined using the procedure proposed by Boys and Foster[13,14] and based on the transformation of the canonical HF orbitals, carried out in such a way as to maximize the distances of the centroids of charge associated with the orbitals, $d_{ij} = [(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{\frac{1}{2}}$, where $q_i = \langle \bar{\varphi}_i | \hat{q} | \bar{\varphi}_i \rangle$ ($q = x, y, z$) represents the coordinate of the centroid associated with the *i*th localized MO $\bar{\varphi}_i$.

Results and Discussion

The molecular structures of the systems considered are shown in Fig. 1. It is assumed that the N(1) atom is the donor centre, directly involved both in the protonation process leading to the pyrazolium cation and in the formation of the co-ordination bond.

The Pyrazole Molecule.—The geometrical structure of the pyrazole molecule was computed using three different basis sets (see above). The optimum geometry parameters are listed in Table 1 and compared with the experimental results obtained from microwave spectra.[15] The errors of the bond lengths and valence angles computed in the present work with respect to the experimental values are, in general, within the ranges 0.01–0.03 Å and 1–2°, respectively. As expected, basis B gives results in acceptable agreement with experiment, thus confirming the results of other studies previously reported.[16] The triple-zeta basis yields values for bond distances very close to those of basis B, but in some cases slightly underestimated with respect to the experimental ones. This effect is certainly due to the lack of electron correlation.

In ref. 16(*a*) a comparison is made also between results of the STO 3-21G and STO 6-21G* bases. The latter, which includes d polarization functions on C and N atoms and p orbitals on H atoms, induces changes in C–C and N–N bond distances of about 0.01 and 0.04 Å, respectively, while changes in valence angles are about 1°. Therefore, all the results obtained with extended-basis sets confirm that basis B is reliable, at least for semiquantitative correlations. The single-zeta basis A gives in general acceptable values of the geometrical parameters: the N–N and C–N distances seem, however, the most basis-set dependent quantities.

A more severe estimate of the quality of the wavefunction determined with different basis sets can be obtained by comparing the modulus and direction of the computed dipole moment with the corresponding experimental values. The dipole moment μ has been computed as equal to 2.15, 2.50 and 2.63 D, for basis A, B and C, respectively. The experimental value is 2.214 D.[15] These data show that μ is a basis-set

Table 1 Optimum geometry (bond lengths in Å, angles in °) and charge distribution of pyrazole[a]

	Basis					Basis			
	A[b]	B[c]	C[d]	Exptl.[e]		A[b]	B[c]	C[d]	Exptl.[e]
N(1)–N(2)	1.384	1.379	1.358	1.351	C(3)–N(2)–N(1)	112.3	111.6	112.0	113.0
N(1)–C(5)	1.330	1.313	1.315	1.332	C(4)–C(3)–N(2)	106.6	106.6	106.9	106.4
N(2)–C(3)	1.379	1.356	1.352	1.360	C(5)–C(4)–C(3)	105.4	105.0	104.8	104.5
C(3)–C(4)	1.354	1.363	1.366	1.374	N(2)–N(1)–C(5)	103.2	104.6	105.0	104.1
C(4)–C(5)	1.424	1.420	1.418	1.417	H–N(2)–N(1)	120.3	119.3	119.0	118.4
N(2)–H	1.023	0.993	0.985	1.002	H–C(3)–N(2)	121.4	122.3	122.1	121.4
C(3)–H	1.081	1.065	1.066	1.082	H–C(4)–C(3)	127.5	127.5	127.7	127.6
C(4)–H	1.076	1.064	1.065	1.080	H–C(5)–C(4)	127.4	127.8	128.8	128.7
C(5)–H	1.081	1.064	1.065	1.083					

		A	B	C			A	B	C
N(1)	s	3.685	3.820	3.751	N(2)	s	3.434	3.650	3.493
	p_σ	2.301	2.320	2.194		p_σ	2.158	2.379	2.271
	p_π	1.166	1.200	1.215		p_π	1.642	1.627	1.632
	q	−0.152	−0.339	−0.160		q	−0.234	−0.655	−0.396
C(3)	s	3.105	3.103	3.103	C(5)	s	3.111	3.126	3.140
	p_σ	1.819	1.698	1.952		p_σ	1.837	1.740	1.976
	p_π	1.040	1.010	1.006		p_π	1.049	1.024	1.001
	q	0.035	0.189	−0.061		q	−0.002	0.110	−0.117
C(4)	s	3.113	3.321	3.104					
	p_σ	1.897	2.007	2.058					
	p_π	1.103	1.140	1.147					
	q	−0.113	−0.468	−0.309					
HN(2)	s	0.769	0.609	0.636	HC(4)	s	0.929	0.759	0.753
	q	0.231	0.391	0.364		q	0.071	0.241	0.247
HC(3)	s	0.915	0.727	0.765	HC(5)	s	0.925	0.742	0.802
	q	0.085	0.273	0.235		q	0.075	0.258	0.198

[a] The orbital occupancies (s, p_σ, p_π) and the net atomic charges (q) have been obtained from Mulliken analysis; σ and π indicate orbitals belonging to the molecular plane or orthogonal to it, respectively. [b] Basis set STO3G. [c] Basis set STO 3-21G. [d] Basis set of triple-zeta quality for valence orbitals. [e] Experimental data from microwave spectra of ref. 14.

dependent quantity, although the results given by the two more extended bases B and C are quite similar. The in-plane principal axes of the inertial tensor approximately point toward C(5) (*b*) and N(1) (*a*), respectively. The centre of mass approximately coincides with the centre of the pentagon. The computed angles that μ forms with *a* are equal to 36.2, 16.9 and 20.6°, for bases A, B and C, respectively. The corresponding value obtained from microwave spectra[15] is 42.2°. Basis A gives values closest to the experimental finding, while the results of bases B and C, still in acceptable agreement with experiment, are slightly worse. However, the success of the minimal basis is most probably due to a fortuitous cancellation of opposite errors and should not be overemphasized. This agrees with the conclusion reached by other *ab initio* studies on Hpz.[17]

These results show that our computational method, even using split-valence basis sets, cannot quantitatively predict all the molecular constants of the pyrazole molecule. However, the trend of the theoretically determined geometry parameters (which do not show a critical basis-set dependence) and the acceptable computed value of the dipole moment suggest that the STO 3-21G basis can be conveniently adopted for an interpretation and explanation of the mutual influences of geometric and electronic factors.

The Pyrazolium Cation and Metal Adducts of Pyrazole.—The structure of the pyrazolium cation H_2pz^+ has been studied using minimal and split-valence basis sets only. The theoretical results reported in Table 2 may be considered as satisfactory as they compare well with the average experimental data, reported in ref. 3 and derived from the analysis of the X-ray data for a large series of pyrazolium salts. Since H_2pz^+ belongs to the C_{2v} point group some molecular parameters must obey symmetry equivalences (see Table 2), which however are not present among the structure parameters reported by Bonati.[3] This can be explained considering that the experimental data concern substituted pyrazolium salts, having symmetry not higher than C_s. This is also the reason why the computed values for H–N(1)–N(2), H–C(3)–N(2) and H–C(5)–C(4) show differences from the experimental as large as 4°, which is too large to be attributed to inadequacies of the present theoretical treatment. On the contrary, the agreement between computed and observed bond lengths is very satisfactory (±0.02 Å), and indicates that steric influences of bulky substituents can mostly affect the valence angles. Finally, one cannot exclude that the symmetry of pyrazolium salts in the solid state is lower than the ideal C_{2v} because of packing forces.

When studying the adducts of pyrazole with transition-metal atoms the following important methodological implications have to be carefully considered. A single-zeta basis cannot be used even for a qualitative description of the co-ordination bond, owing to the impossibility of representing the ligand-to-metal charge transfer or polarization of the ligand lone pair in a proper way. In the absence of a realistic description of such effects it is obviously difficult to account for the structural modifications undergone by the ligand groups in the co-ordination process. This is the reason why the adducts of pyrazole have been investigated using only the split-valence basis set for all the atoms.

In the metal adducts X(Hpz) the pyrazole ligand essentially acts as a donor through the lone pair located on the N(1) atom. The electronic structure of Hpz can therefore be considered either as simply perturbed by a positively charged centre, or affected by the presence of an electron-withdrawing (Lewis-acid) group. In the first case it is expected that only charge redistribution within the ligand can occur. In the second case, the formation of the adduct is also accompanied by charge transfer. The two possible perturbations have been simulated in different ways. In the first case the structure of the pyrazole molecule was computed in the presence of a unit positive point charge (Q^+), located at a fixed (not optimized) distance of 3.0 Å

Table 2 Optimum geometry (bond lengths in Å, angles in °) and charge distribution of the pyrazolium cation[a]

	Basis				Basis		
	A	B	Exptl.[b]		A	B	Exptl.[b]
N(1)–N(2)	1.384	1.375	1.365	C(3)–N(2)–N(1)	108.1	108.3	109.0
N(1)–C(5)	1.356	1.333	1.351	C(4)–C(3)–N(2)	108.6	108.7	107.8
N(2)–C(3)	1.356	1.333	1.334	C(5)–C(4)–C(3)	106.6	106.0	107.6
C(3)–C(4)	1.390	1.384	1.384	N(2)–N(1)–C(5)	108.1	108.3	108.5
C(4)–C(5)	1.390	1.384	1.386	H–N(1)–N(2)	121.7	121.5	117.0[c]
N(1)–H	1.033	1.001		H–C(3)–N(2)	120.8	120.5	122.3[c]
C(3)–H	1.090	1.065		H–C(4)–C(3)	126.7	127.0	
C(4)–H	1.079	1.062		H–C(5)–C(4)	130.6	129.7	131.9[c]
C(5)–H	1.090	1.065		H–N(2)–N(1)	121.7	121.5	
N(2)–H	1.033	1.001					

		A	B			A	B			A	B
N(1)	s	3.429	3.652	C(3)	s	3.133	3.125	HN(1)	s	0.682	0.538
	p_σ	2.140	2.317		p_σ	1.862	1.741		q	0.318	0.462
	p_π	1.596	1.606		p_π	0.864	0.839	HC(3)	s	0.831	0.625
	q	−0.165	−0.575		q	0.141	0.295		q	0.169	0.375
N(2)	s	3.429	3.652	C(4)	s	3.110	3.338	HC(4)	s	0.854	0.660
	p_σ	2.140	2.317		p_σ	1.883	2.010		q	0.146	0.340
	p_π	1.596	1.606		p_π	1.082	1.109	HC(5)	s	0.831	0.625
	q	−0.165	−0.575		q	−0.074	−0.457		q	0.169	0.375
				C(5)	s	3.133	3.125	HN(2)	s	0.682	0.538
					p_σ	1.862	1.741		q	0.318	0.462
					p_π	0.864	0.839				
					q	0.141	0.295				

[a] See footnotes *a–c* in Table 1. [b] Experimental data from ref. 3 and refs. therein. [c] The experimental values are for substituted pyrazole ligands. The values for H–C–N, H–C–C and H–N–N angles are compared with those for C–C–N, C–C–C and C–N–N angles, respectively.

from the N(1) donor atom. In the second case two X(Hpz) systems were considered in which the X unit is represented by a CuF group or by a Cu^+ ion. In the third species X(Hpz) the positively charged centre is a sodium cation Na^+ with bonding characteristics different from those of a copper(I) centre.

The data reported in Table 3 allow some important considerations. First, the charge donated from the pyrazole to the M group *via* a σ mechanism amounts to 0.076, 0.106, 0.116 and 0.000 e for X = CuF, Cu^+, Na^+ and Q^+, respectively. The π system of pyrazole is little involved in the charge transfer as only 0.014 and 0.006 e are back donated to the ligand in the CuF and Cu^+ adducts, respectively. On the contrary, in the case of the Na^+ adduct 0.021 e is transferred to the metal cation from the Hpz π sextet, a fact which may be explained by the presence on Na^+ of low-lying empty 3p orbitals with appropriate symmetry, and by its high acidity.

The net atomic charge on N(1) of co-ordinated pyrazole is always negative and larger (ranging from −0.48 to −0.61) than that computed for the free Hpz molecule (−0.34), despite the fact that N(1) is the donor centre in the adducts. Therefore, the large negative charge of N(1) is due to the strong polarizing effect of the centre CuF, Cu^+, Na^+ or Q^+. When the electron distribution in co-ordinated Hpz is compared with that of the free molecule it can be observed (see Tables 1 and 3) that the largest variations occur for N(1), which increases in both σ and π electrons, and, as a consequence, also its negative charge. In particular, the increase in p_π of N(1) (0.16, 0.22, 0.17 and 0.09 for X = CuF, Cu^+, Na^+ and Q^+) is important and always larger than the increase in the σ orbitals. It is evident that the polarizing effect of the positively charged centre involves both the σ and π electrons in the vicinity of the N(1) atom.

Interesting observations can be made when the theoretically determined geometries of the X(Hpz) complexes are compared with the best geometry of the free Hpz ligand. The variations of the bond lengths δ(A–B) are very regular: δ[N(1)–N(2)], δ[N(1)–C(5)] and δ[C(3)–C(4)] are always positive and assume maximum values of 0.013, 0.011 and 0.006 Å, respectively for X = Na^+. On the contrary, δ[N(2)–C(3)] and δ[C(4)–C(5)] are always negative, with a maximum value again for X = Na^+ (−0.010 and −0.016 Å, respectively). The same trend has also been found for the H_2pz^+ cation which, however, is characterized by larger variations {*e.g.* 0.021 Å for δ[C(3)–C(4)] and −0.036 Å for δ[C(4)–C(5)]}. The N–H and C–H distances of the co-ordinated Hpz do not show modifications with respect to the free Hpz molecule larger than 0.002 Å. Analogously the computed variations δ(A–B–C) are within the range 0–1.0°, with the exception of δ[H–N(2)–N(1)] which has a deviation of about 2.5° in $Cu(Hpz)^+$.

The fact that it is possible to point out regularities in the geometrical distortions within the co-ordinated pyrazole and variations in the electronic distribution does not mean that it is easy to establish a meaningful correlation. It is evident that only N(1) is affected by a major charge reorganization, but probably not enough significantly to influence the bond distances. In addition, in all the adducts considered the X group acts as a Coulomb perturber, causing effects which overlap those of a pure co-ordination bond and which cannot be clearly separated.

The computed structural modifications δ(A–B) and δ(A–B–C) are quite small with respect to the free Hpz molecule, and it is therefore not surprising that such a trend has never before been pointed out on the basis of the experimental data. Such small effects could easily be masked by experimental inaccuracy, or cancelled by packing or steric solid-state forces acting in the opposite direction.

Finally, our results concerning the X(Hpz) adducts, especially those of $Na(Hpz)^+$, are in agreement with the findings of Alcamí *et al.*[16c] obtained for the $Li(Hpz)^+$ complex.

Pyrazolate Compounds.—The structure of the free pyrazolate anion (C_{2v} symmetry) was investigated only with the STO 3-21G basis (see Table 4).

The pyrazolate compounds X(pz) considered are those with X = Na^+, Cu^+ or $Cu(NH_3)^+$. Generally, comparison with available experimental data[3] shows the theoretically determined molecular geometries (see Table 4) to be satisfactory. It is important to note that the N(1)–C(5) and N(2)–C(3) distances, which are symmetry equivalent in the free pyrazolate anion, become different in the salts by about 0.02 Å, in

Table 3 Optimum geometry (bond lengths in Å, angles in °) and charge distribution of metal adducts of pyrazole[a]

	CuF(Hpz)	Cu(Hpz)$^+$	Na(Hpz)$^+$	Q(Hpz)$^+$	Exptl.[b]
N(1)–N(2)	1.378	1.389	1.392	1.387	1.354
N(1)–C(5)	1.315	1.322	1.324	1.316	1.333
N(2)–C(3)	1.347	1.347	1.346	1.354	1.346
C(3)–C(4)	1.367	1.369	1.369	1.364	1.362
C(4)–C(5)	1.409	1.402	1.404	1.413	1.386
N(2)–H	0.995	0.994	0.995	0.993	
C(3)–H	1.065	1.065	1.065	1.065	
C(4)–H	1.063	1.063	1.063	1.063	
C(5)–H	1.065	1.066	1.066	1.066	
N(1)–Cu	1.895	1.958			
N(1)–Na			2.223		
Cu–F	1.749				
C(3)–N(2)–N(1)	110.6	110.3	110.7	111.1	111.5
C(4)–C(3)–N(2)	107.6	107.9	107.8	107.5	106.7
C(5)–C(4)–C(3)	105.2	105.2	105.2	105.0	106.3
N(2)–N(1)–C(5)	105.5	105.1	104.6	104.5	105.3
H–N(2)–N(1)	119.9	121.8	121.6	121.2	
H–C(3)–N(2)	122.0	121.9	122.0	122.1	122.1[c]
H–C(4)–C(3)	127.5	127.4	127.5	127.6	126.9[c]
H–C(5)–C(4)	128.1	127.4	127.5	127.3	129.3[c]

		CuF(Hpz)	Cu(Hpz)$^+$	Na(Hpz)$^+$	Q(Hpz)$^+$
N(1)	s	3.758	3.747	3.775	3.786
	p_σ	2.443	2.437	2.360	2.400
	p_π	1.357	1.424	1.372	1.297
	q	−0.558	−0.609	−0.507	−0.483
C(3)	s	3.107	3.118	3.119	3.113
	p_σ	1.712	1.727	1.727	1.714
	p_π	0.957	0.915	0.924	0.962
	q	0.224	0.240	0.230	0.211
C(4)	s	3.323	3.328	3.325	3.324
	p_σ	2.006	2.005	2.001	2.006
	p_π	1.139	1.122	1.124	1.126
	q	−0.469	−0.454	−0.450	−0.455
HC(3)	s	0.696	0.666	0.673	0.691
	q	0.304	0.334	0.327	0.309
HC(4)	s	0.730	0.698	0.704	0.722
	q	0.270	0.302	0.296	0.278

		CuF(Hpz)	Cu(Hpz)$^+$	Na(Hpz)$^+$	Q(Hpz)$^+$
N(2)	s	3.648	3.646	3.649	3.647
	p_σ	2.355	2.350	2.362	2.367
	p_π	1.617	1.628	1.627	1.636
	q	−0.620	−0.624	−0.638	−0.650
C(5)	s	3.120	3.129	3.133	3.130
	p_σ	1.741	1.760	1.763	1.761
	p_π	0.944	0.917	0.932	0.979
	q	0.196	0.194	0.172	0.131
HC(5)	s	0.700	0.692	0.701	0.727
	q	0.300	0.308	0.299	0.273
HN(2)	s	0.585	0.591	0.592	0.614
	q	0.415	0.409	0.408	0.386

		CuF(Hpz)	Cu(Hpz)$^+$
Cu	s	6.662	6.159
	p_σ	7.996	7.994
	p_π	4.000	4.000
	d_σ	7.671	7.953
	d_π	1.989	1.994
	q	0.681	0.900

		CuF(Hpz)
F	s	3.978
	p_σ	3.768
	p_π	1.997
	q	−0.742

		Na(Hpz)$^+$
Na	s	4.069
	p_σ	4.046
	p_π	2.021
	q	0.863

[a] See footnote *a* in Table 1. [b] Experimental data from ref. 3 and refs. therein. [c] See footnote *c* in Table 2.

agreement with experimental observation. On the contrary, the C(3)–C(4) and C(4)–C(5) distances, which are nearly identical according to experiment, differ by about 0.02 Å in the theoretical estimate. Such computed differences, although small, are probably of physical relevance since they have been systematically found for all the species considered.

The bond formation in the pyrazolate salts can be interpreted in terms of a donation from pz$^-$ to the positively charged group. This amounts to 0.23 and 0.20 e in the case of X = Cu$^+$ and CuNH$_3$$^+$, respectively. The fact that also in this case the formation of the complex is essentially controlled by the σ-donation mechanism is confirmed by a very low charge (about 0.006 e) back-donated to the π* MOs of the ligand.

Analogously, when the interaction between pz$^-$ and Na$^+$ is considered the σ ligand-to-metal donation is found to be 0.19 e. However, in this case the bonding π MOs of pz$^-$ have a total occupancy equal to 5.951, which again shows that also the π system may act as weak donor in the presence of a strong acid centre.

In all three pyrazolate salts it is evident that a charge transfer from the ligand to the metal centre occurs which partially reduces the ionicity of the X$^+$–pz$^-$ interaction. The largest variations in orbital occupancies in X(pz) with respect to pz$^-$ occur again for p_π of N(1), which increases by 0.16, 0.25 and 0.23 for X = Na$^+$, Cu$^+$ and Cu(NH$_3$)$^+$, respectively. Variations in σ-orbital occupations are much smaller for all atoms. Therefore, the increase in negative charge on N(1) is essentially due to polarization of the π electrons.

When the constraint imposed upon the X–N(1)–N(2) angle (120°) is removed, the best arrangement of the Na$^+$ ion is that corresponding to a η^2 co-ordination, *i.e.* a symmetrical interaction of Na$^+$ with both the N atoms. The optimized distances are N(1)–Na = N(2)–Na 2.132 Å, and the complex has C_{2v} symmetry. Such a configuration is more stable than the σ one by about 66 kJ mol^{-1}. Similar calculations carried out on the Cu$^+$ adduct (but now imposing C_{2v} symmetry) gave a η^2 arrangement [N(1)–Cu = N(2)–Cu 2.100 Å] characterized by an energy 23 kJ mol^{-1} higher than that of the σ configuration. Therefore the η^2 form is preferred only for Na$^+$, while probably being a saddle point for Cu$^+$.

Table 4 Optimum geometry (bond lengths in Å, angles in °) and charge distribution of metal pyrazolates[a]

	pz^-	Na(pz)	Cu(pz)	Cu(NH$_3$)(pz)	Exptl.[b]
N(1)–N(2)	1.385	1.395	1.387	1.387	1.363
N(1)–C(5)	1.342	1.357	1.352	1.350	1.354
N(2)–C(3)	1.342	1.323	1.322	1.324	1.331
C(3)–C(4)	1.398	1.406	1.407	1.406	1.373
C(4)–C(5)	1.398	1.376	1.375	1.377	1.371
C(3)–H	1.071	1.067	1.066	1.067	
C(4)–H	1.069	1.065	1.065	1.065	
C(5)–H	1.071	1.070	1.068	1.068	
N(1)–Cu		1.859	1.854		
N(1)–Na	2.100				
C(3)–N(2)–N(1)	107.4	107.2	106.4	106.6	105.5
C(4)–C(3)–N(2)	111.1	111.2	111.4	111.3	111.3
C(5)–C(4)–C(3)	103.0	103.9	104.0	103.9	105.3
N(2)–N(1)–C(5)	107.4	107.4	108.6	108.5	109.9
H–C(3)–N(2)	121.0	120.8	120.7	120.7	119.9[c]
H–C(4)–C(3)	128.5	128.0	128.0	128.0	125.0[c]
H–C(5)–C(4)	127.9	128.2	128.7	128.0	131.3[c]

		pz^-	Na(pz)	Cu(pz)	Cu(NH$_3$)(pz)			pz^-	Na(pz)	Cu(pz)	Cu(NH$_3$)(pz)
N(1)	s	3.803	3.763	3.728	3.732	N(2)	s	3.803	3.803	3.807	3.805
	p_σ	2.440	2.464	2.511	2.527		p_σ	2.440	2.386	2.378	2.381
	p_π	1.245	1.409	1.493	1.473		p_π	1.245	1.235	1.224	1.224
	q	−0.488	−0.636	−0.732	−0.731		q	−0.488	−0.424	−0.408	−0.409
C(3)	s	3.122	3.126	3.125	3.124	C(5)	s	3.122	3.121	3.110	3.108
	p_σ	1.711	1.736	1.736	1.733		p_σ	1.711	1.727	1.716	1.711
	p_π	1.132	1.061	1.059	1.067		p_π	1.132	1.062	0.053	1.056
	q	0.035	0.077	0.080	0.076		q	−0.035	0.091	0.121	0.125
C(4)	s	3.295	3.305	3.308	3.306						
	p_σ	1.955	1.980	1.987	1.985						
	p_π	1.246	1.184	1.177	1.186						
	q	−0.496	−0.469	−0.472	−0.477						
HC(3)	s	0.861	0.788	0.779	0.788	HC(5)	s	0.861	0.804	0.791	0.797
	q	0.139	0.212	0.221	0.212		q	0.139	0.196	0.209	0.203
HC(4)	s	0.876	0.803	0.794	0.803						
	q	0.124	0.197	0.206	0.197						

		Na(pz)			Cu(pz)	Cu(NH$_3$)(pz)			Cu(NH$_3$)(pz)
Na	s	4.113	Cu	s	6.401	6.622	N(NH$_3$)	s	3.713
	p_σ	4.077		p_σ	7.991	7.994		p	4.252
	p_π	2.049		p_π	4.000	4.000		q	−0.96
	q	0.756		d_σ	5.838	5.702	H(NH$_3$)	s	0.641[d]
				d_π	3.995	3.989		q	0.359[d]
				q	0.775	0.693			

[a] See footnote *a* in Table 1. [b] Experimental values from ref. 3 and refs therein. [c] See footnote *c* in Table 2. [d] Value averaged over non-equivalent hydrogen atoms.

All attempts at correlating the geometry distortion within the ligand [in particular the modifications of N(1)–C(5) and N(2)–C(3) as well as C(3)–C(4) and C(4)–C(5) with respect to the free pz^- anion] with the extent of the σ donation were unsuccessful.

The fact that the interaction involving the pz^- anion is dominated by Coulomb forces is confirmed by a set of calculations in which the X^+ cation is substituted with a unit point charge (Q^+) placed 2.0 and 3.0 Å from N(1) [Q–N(1)–N(2) 120°]. The charge is able to generate electric fields bracketing those generated by the metal atoms in Cu(pz) and Cu(NH$_3$)(pz), which carry positive charges of 0.775 and 0.693, respectively. It has been found that the point charge is able to produce geometry distortions very similar to those computed for the pyrazolate salts, in which the polarization effects are also accompanied by (relatively small) charge transfers.

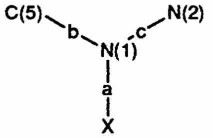
In comparison with free pz^- the geometric parameters show very regular variations for all the three species considered. In particular δ[N(1)–N(2)], δ[N(1)–C(5)] and δ[C(3)–C(4)] are positive while δ[N(2)–C(3)] and δ[C(4)–C(5)] are negative. The sodium salt (σ structure) is characterized by the largest modifications. All other internal coordinates of pz^- are characterized by negligible δ(A–B) or δ(A–B–C): for instance, the δ(A–H) [A = C(3), C(4) or C(5)] are of the order of 0.001 Å while δ(A–B–C) involving hydrogen atoms are always smaller than 1°. Finally, it is worth noting that the geometries of Cu(pz) and Cu(NH$_3$)(pz) are extremely similar.

The Electron Distribution around the Co-ordination Centre described with the Help of LMOs.—The method of Boys and Foster[13] for generating LMOs was applied to the following species: Hpz, H_2pz^+, $Cu(Hpz)^+$, Na(Hpz), CuF(Hpz) and Cu(pz).

In the pyrazole derivatives the N(1) atom is always involved in a framework of σ bonds which have only approximate trigonal symmetry. The N(2)–N(1)–C(5) angle can vary within a relatively small range, 107–110°, while the chemical inequivalence of the substituents on N(1) can induce differences in the X–N(1)–C(5) and X–N(1)–N(2) angles as large as 9–15°. This latter point has already been recognized as the most important structural feature of the co-ordinated Hpz ligand.[3]

It is natural to attempt a correlation of the values of the

Table 5 Geometry (bond lengths in Å, angles in °) of the centroids of localized molecular orbitals and atoms around the co-ordination centre in pyrazole systems



Distances atom–centroid

	N(1)–a	X–a	N(1)–b	C(5)–b	N(1)–c	N(2)–c
Hpz	0.38		0.58	0.73	0.73	0.65
H_2pz^+	0.57	0.43	0.56	0.77	0.69	0.69
CuF(Hpz)	0.44	1.46	0.58	0.74	0.72	0.66
$Cu(Hpz)^+$	0.46	1.50	0.58	0.75	0.72	0.67
$Na(Hpz)^+$	0.43	1.80	0.58	0.75	0.73	0.67
Cu(pz)	0.52	1.34	0.60	0.76	0.67	0.72

Approximate composition of the LMOs expressed as %s[N(1)] *

	LMO on bond		
	N(1)–X	N(1)–C(5)	N(1)–N(2)
Hpz	53.2	38.6	29.7
H_2pz^+	43.2	43.8	35.8
CuF(Hpz)	48.1	40.2	31.3
$Cu(Hpz)^+$	47.1	41.0	31.8
$Na(Hpz)^+$	53.1	39.8	36.9
Cu(pz)	43.2	39.1	38.4

Distances centroid–centroid and valence angles

	a–b	a–c	b–c	C(5)–N(1)–X	N(2)–N(1)–X	N(2)–N(1)–C(5)
Hpz	0.89	0.99	1.05	133.8	121.6	104.6
H_2pz^+	1.03	1.10	1.02	130.3	121.5	108.2
CuF(Hpz)	0.94	1.01	1.03	134.5	120.0	105.5
$Cu(Hpz)^+$	0.96	1.03	1.03	134.9	120.0	105.1
$Na(Hpz)^+$	0.94	1.02	1.04	135.4	120.0	104.6
Cu(pz)	1.02	1.03	1.04	131.4	120.0	108.6

* See text for definition of %s[N(1)].

computed valence angles around N(1) with the composition of its hybrid orbitals or, equivalently, with the compositon of each LMO associated with the corresponding bonds. Such an analysis requires some preliminary consideration concerning the physical meaning which can be derived from an analysis based on LMOs.

According to the definition of Boys and Foster, each LMO is a function maximally localized in space, minimizing the Coulomb and exchange interaction with all other LMOs. In addition the two electrons occupying a given LMO, of opposite spin, are subjected only to Coulomb, not to exchange, forces. Therefore, to a good approximation, the mutual interaction between localized electron pairs can be discussed in terms of classic electrostatics, and qualitatively predicted if their centres of charge are known. These are the underlying principles of the VSEPR approach.[4] This approach has been introduced and applied in a substantially empirical fashion, aiming at deriving concepts on the spatial distribution of the electron pairs and their mutual interactions from known molecular geometries.

On the contrary, in the present context the discussion will be based on purely theoretical data, *i.e.* the geometrical features of the bonds will be explained in a very natural way on the basis of the electron distribution.

Each LMO can be identified by its centre of charge (see above) and composition in terms of atomic functions. Owing to the localized nature of the orbitals, the atomic functions may be conveniently chosen as hybrid orbitals having the desired spatial directionality. Accordingly, assuming for simplicity a single-zeta basis, the LMO describing the σ bond between atoms A and B can be written as $\varphi_{AB} = c_A h_A + c_B h_B$ with $c_A^2 + c_B^2 + 2c_A c_B \langle h_A | h_B \rangle = 1$. The sp^2-type hybrid orbital h_A (presumed lying in the *xy* plane) is defined as $h_A = a_{sA} | s_A \rangle + a_{xA} | p_{xA} \rangle + a_{yA} | p_{yA} \rangle$, with $a_{sA}^2 + a_{xA}^2 + a_{yA}^2 = 1$. For an ideal sp^2 hybrid participating in a purely covalent, homonuclear bond, one obviously has $a_{sA}^2 = \frac{1}{3}$ and $a_{xA}^2 + a_{yA}^2 = \frac{2}{3}$. The two electrons described by φ_{AB} can be partitioned according to $2 = Q_A + Q_B$, where $Q_A/2 = c_A^2 + c_A c_B \langle h_A | h_B \rangle$. The population of the s orbitals centred on A is clearly equal to $Q_{sA}/2 = c_A^2 a_{sA}^2 + c_A c_B a_{sA} (a_{sB} \langle s_A | s_B \rangle + a_{xB} \langle s_A | p_{xB} \rangle + a_{yB} \langle s_A | p_{yB} \rangle)$, and depends not only on the s character of h_A but also on the s–p nature of h_B, and on related overlap integrals. The relative (percentage) contribution of s orbitals on A can therefore be defined as $\% \, s(A) = 100 Q_{sA}/Q_A$.

For the sake of brevity only data concerning three LMOs will be discussed, that is those associated with the bonds N(1)–X, C(5)–N(1) and N(1)–N(2) obtained by localizing all the σ (in plane) MOs with a prevailing valence character. Here X either represents the Lewis-acid centre or identifies the direction of the lone pair on N(1) in Hpz. The centroids of the three LMOs will be referred to as the points a, b and c, respectively (see Table 5). The composition of the LMOs will be discussed in terms of the %s [N(1)] quantity.

For the C(5)–N(1) bond, in the series of compounds X(Hpz) (X = CuF, Cu^+ or Na^+) the distance b–N(1) is always equal to 0.58 Å while b–C(5) varies in the range 0.74–0.76 Å. For the N(1)–N(2) bond the values of the distances c–N(1) and c–N(2) show that the centroid of charge is located closer to the N(2) atom. The N(1)–X bond is characterized by a value of a–N(1), much smaller in general than a–X but larger than the corresponding distance in Hpz (0.38 Å). This is true for X(Hpz) (X = CuF, Cu^+ or Na^+) and for Cu(pz), while in H_2pz^+ the a–N(1) distance is longer than a–X (X = H^+). The largest variations of a–N(1) with respect to the value found in Hpz occur in H_2pz^+ and Cu(pz), a fact which can easily be interpreted as being due, in the first case, to the strong polarizing character of H^+ and in the second case to the high polarizability of the N(1) lone pair in pz^- due to the excess of charge.

The %s[N(1)] quantity for corresponding bonds is very similar for the complexes X(Hpz) (X = CuF, Cu^+ or Na^+). Values higher than 33 (which would correspond to an ideal sp^2 hybrid) have been computed for N(1)–X and N(1)–C(5), while the values relative to the N(1)–N(2) bond are always smaller than those of N(1)–X and N(1)–C(5). Again the H_2pz^+ and the Cu(pz) species show large differences from the X(Hpz) adducts. Indeed, the %s[N(1)] value of the N(1)–X bond increases from 43 in X(pz) and H_2pz^+ to about 47–53 in the Hpz adducts. Therefore, in H_2pz^+ and Cu(pz) the polarization (and expansion) of the N(1) lone pair is also accompanied by a decrease in the s contribution to the hybrid orbital, *i.e.* to an enhanced $s \longrightarrow p$ electron promotion.

Table 5 clearly shows that for all the considered compounds the %s[N(1)] values for three bonds follow the rule N(1)–X > N(1)–C(5) > N(1)–N(2), *i.e.* a sequence opposite to the electronegativity trend of the substituents on N(1): the larger is the electronegativity the smaller is the s character of the hybrid. This is a theoretical confirmation of Bent's rule, originally proposed empirically and applied to a completely different class of compounds.[18]

The fact that the b–C(5), b–N(1), c–N(1) and c–N(2) distances are very similar in all the X(Hpz) adducts, as well as the associated %s[N(1)] quantities, confirms that the nature (polarization or ionicity characters) of the two bonds is very similar, a fact which reflects the closeness of the bond lengths, discussed above.

The trend in the values of the angles formed by bonds around N(1) can be analysed in terms of the distances between the points a, b and c. Alternatively, one can also consider the distances a–N(1), b–N(1) and c–N(1). The value of the angle C(5)–N(1)–N(2) cannot correlate only with b–N(1) and c–N(1), since the rigidity of the ring (also determined by the π-electron system) forces it to be close to 108°. The two angles C(5)–N(1)–X and N(2)–N(1)–X are, on the contrary, much more free. For nearly equal polarities of the C(5)–N(1) and N(2)–N(1) bonds, the two angles would be expected to assume a value of about 126°. Our results show that C(5)–N(1)–X and N(2)–N(1)–X have values in the ranges 130–135 and 120–122°, respectively. The fact that C(5)–N(1)–X is always bigger than N(2)–N(1)–X is just a consequence of the fact that c–N(1) is larger than b–N(1), which means that the electron pairs located at b and a have stronger repulsion than those located at c and a.

Conclusion

From the set of theoretically determined geometry parameters of the free and co-ordinated pyrazoles the following general rules can be obtained: (1) N(1)–C(5) is always smaller than N(2)–C(3) by about 0.02–0.04 Å; analogously C(3)–C(4) is always shorter than C(4)–C(5) by about 0.03–0.06 Å; (2) when the bond distances of co-ordinated Hpz or pz^- are compared with those of the corresponding free neutral or anionic ligand the distances N(1)–N(2), N(1)–C(5) and C(3)–C(4) are slightly elongated while N(2)–C(3) and C(4)–C(5) are shorter; (3) C(5)–N(1)–X is always larger than N(2)–N(1)–X and both are larger than the internal angle C(5)–N(1)–N(2) [on the basis of the interaction between electron pairs located on C(5)–N(1) and N(1)–N(2) the angle C(5)–N(1)–N(2) would be expected to be larger; its low value is due to the rigidity of the cyclic structure]; (4) within the pz^- and Hpz rings in free or co-ordinated form, the smallest angle is always C(5)–C(4)–C(3); (5) in all the considered pyrazolate salts it has been found that N(2)–N(1)–C(5) > C(3)–N(2)–N(1). [Note however that the two angles are nearly identical in Na(pz). The same relation N(2)–N(1)–C(5) > C(3)–N(2)–N(1) is also observed for the metal adducts X(Hpz), while the opposite holds true for free Hpz.]

The above rules parallel those found by Bonati[3] from experimental X-ray data. The only exception is rule (2) which could not have been derived, probably because of limited accuracy in the experimental data.

Our analysis has shown that the basic concepts of the VSEPR approach and Bent's rule are valid for qualitative considerations concerning the interplay between the location of the electron pairs and geometry variations. More precise information can be obtained when the exact spatial position of the centroids of charge can be computed. In this sense the use of the LMOs seems to be very necessary, especially when bonding features are to be discussed in terms of hybrid orbitals, Note, however, that the s–p composition of the hybrids can be substantially different from that inferred from only a qualitative estimate of the valence angles involved. The present study has confirmed that Hpz and pz^- ligands are very rigid rings from a geometrical point of view, but not from an electronic point of view. They experience a non-negligible charge rearrangement upon co-ordination, involving in an important way also the π sextet. This contradicts the assumption that only the N(1) lone pair is affected by the presence of a Lewis acid.

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