do not necessarily occur at HDS active sites. The relative HDS reactivities of methylthiophenes also increase with the number of methyl groups: T (1.0) < 2-MeT (1.5) < 3-MeT (1.9) < 2,5-Me_2T (2.0).[20] Another HDS study[21] also over Co–Mo/Al_2O_3 shows a similar trend: T ~ 2-MeT < 3-MeT. Thus, methyl groups on the α-carbons do not reduce the reactivity of thiophenes but actually enhance it. These results were interpreted to mean that S-coordination of thiophene was unlikely to be important in HDS since α-methyl groups were thought to inhibit sterically the adsorption of thiophenes and should therefore reduce their HDS rates.

Steric inhibition would not be a problem for η^5-coordinated thiophenes. The η^5 binding mode accounts for the stronger adsorption of thiophenes with increasing methyl substitution;[5] it also explains relative rates of thiophene proton exchange with deuterium.[22] In addition, η^5 adsorption and reactivity provide a reasonable and useful mechanism for thiophene HDS.[4,23] Thus, η^5-coordination offers reasonable explanations for several types of thiophene behavior on HDS catalysts.

However, results of the studies presented in this paper indicate that S-coordination is not as unreasonable as previously assumed. Since 2,5-methyl groups do not sterically accelerate thiophene dissociation from $Cp'(CO)_2Re(Th)$ but inhibit it, this suggests that 2,5-methyl groups strengthen the Re–thiophene bond. A stronger metal–thiophene bond would presumably also increase equilibrium adsorption constants for methyl-substituted thiophenes on HDS catalysts, as observed.[15] Thus, one can account for the relative order of methylthiophene binding to HDS catalysts by assuming either η^5- or S-thiophene coordination. However, at this time, there is no evidence to suggest that S-binding promotes thiophene C–S bond cleavage as there is in η^5-thiophene complexes. So, the η^5 adsorption mode still offers the more complete explanation of thiophene reactivity on HDS catalysts.

Registry No. $Cp(CO)_2Re(T)$, 131758-95-7; $Cp(CO)_2Re(3\text{-}MeT)$, 131758-96-8; $Cp(CO)_2Re(2\text{-}MeT)$, 131758-97-9; $Cp(CO)_2Re(2,5\text{-}Me_2T)$, 131758-98-0; $Cp(CO)_2Re(Me_4T)$, 131758-99-1; $Cp(CO)_2Re(DBT)$, 131759-00-7; $Cp^*(CO)_2Re(3\text{-}MeT)$, 131759-01-8; $Cp^*(CO)_2Re(2,5\text{-}Me_2T)$, 131759-02-9; PPh_3, 603-35-0.

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Crystallographic Study of the Stretching of the Copper–Nitrogen Bond in the Complex of a Large-Cavity Reinforced Macrocycle

Gary Pattrick and Robert D. Hancock*

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In previous papers[1-3] the metal ion selectivity of the saturated tetraazamacrocycles has been investigated, and the results have suggested that these ligands are too flexible to exert genuine size-match selectivity. Metal ions that are too large for the macrocyclic cavity are simply accommodated in conformers where they lie outside the macrocyclic cavity and appear to suffer no significant drops in complex stability because of this. The factor that actually controls metal ion size selectivity is the size of the chelate ring, as has been extensively discussed.[4,5] In order to try to make the macrocyclic ring of saturated macrocycles more rigid, and so perhaps exert something more nearly corresponding to size-match selectivity, we have studied the *reinforced* macrocycles. These macrocycles, first synthesized by Wainwright et al.,[6,7] have double bridges between at least one pair of adjacent nitrogen donors, giving piperazine, homopiperazine, or DACO (1,5-diazacyclooctane) type bridges. We have previously reported structures and coordinating properties of complexes of B-12-$aneN_4$,[8,9] B-18-$aneN_4O_2$ and B_2-18-$aneN_4O_2$,[10] and HA-2,2-HP,

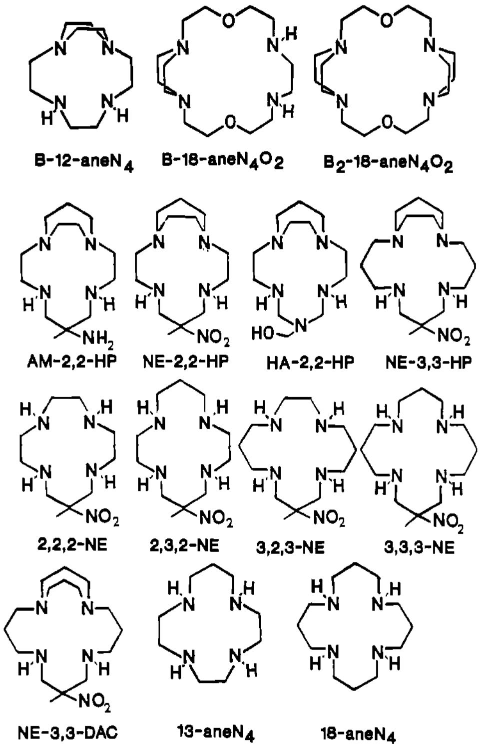
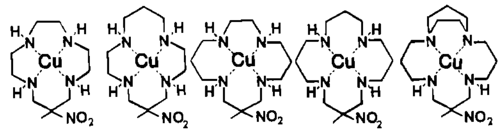


Figure 1. Ligands discussed in this paper.



	2,2,2-NE	2,3,2-NE	3,2,3-NE	3,3,3-NE	NE-3,3-HP
Cu-N (Å):	(1.95)	2.00	2.04	2.02	2.09
best fit M-N for cavity (Å):	1.92	2.07	2.15	2.22	
νd-d (cm^{-1}):	18870	19570	17480	16560	16580
d out of plane (Å):	0.35	0.00	0.14	0.43	0.36

Figure 2. Mean Cu–N bond lengths and d–d band energies in complexes of macrocycles derived from template reaction of tetraamine complexes with nitroethane and formaldehyde. Also shown is the M–N bond length that fits the macrocycle with the least steric strain, as calculated by Busch et al.[13] for the unsubstituted analogues, i.e. 13-$aneN_4$ through 16-$aneN_4$ (Figure 1). Data are from ref 12 and this work. The very long Cu–N bond length in the complex of the reinforced macrocycle NE-3,3-HP (this work) should be noted.

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NE-2,2-HP, and AM-2,2-HP[11] (see Figure 1 for key to ligand abbreviations).

A particular result of the flexibility of the macrocyclic ring in saturated macrocycles is that the metal ion is usually able to achieve close to normal M–L bond lengths, even in cases where the mismatch in size of metal ion and cavity is large. This is well illustrated by the Cu–N bond lengths for the set of tetraazamacrocyclic complexes recently reported by Lawrance et al.,[12] shown in Figure 2.

It is seen that in spite of the variation in cavity size, based on the calculations of De Hayes and Busch[13] for the unsubstituted analogues, the variation in Cu–N bond length is quite small. We have placed the rather short reported[12] Cu–N bond length for the complex with 2,2,2-NE in parentheses because in the drawing of the complex shown by these authors, there is very extensive disorder indicated by the large thermal ellipsoids, which is found[14] to lead to apparently short bond lengths. The Cu–N bond in this complex is quite probably shorter than usual, but possibly by not as much as suggested by the crystal structure. The strain-free Cu–N bond length is[4] 2.00 Å in completely square-planar complexes of Cu(II) and about 2.03 Å with weakly coordinating axial ligands present.

The synthetic route to the macrocycles of Lawrance et al.[12] is very attractive, involving a one-step condensation of the parent Cu(II) complex with nitroethane and formaldehyde. In order to see whether structural reinforcement really can increase the rigidity of a large macrocyclic ring and promote M–L bond stretching, the Cu(II) complex of the reinforced macrocycle NE-3,3-HP was synthesized by the method of Lawrance et al., and its structure was determined.

Experimental Section

Synthesis of [Cu(NE-3,3-HP)Cl](ClO$_4$). The parent tetraamine *N*,*N'*-bis(3-aminopropyl)homopiperazine (3,3-HP) was synthesized as described previously.[15] The copper complex of the macrocycle was synthesized according to the template reaction of Lawrance et al. To a stirred refluxing solution of 3,3-HP (1.5 g), $Cu(NO_3)_2 \cdot 3H_2O$ (1.69 g), nitroethane (0.8 mL), and triethylamine (1.0 mL) in methanol (25 mL) was added dropwise over 2 h a solution of 37% aqueous formaldehyde (4 mL) in methanol (15 mL). After the addition of 500 mL of water, the diluted solution was filtered and absorbed onto a column of Indion SP3 cellulose ion-exchange resin. Elution with 0.15 M NaCl produced two products, one of which was the unreacted parent complex. The required product, which eluted first, was recovered by evaporation of the solvent, separation of the product from NaCl by uptake in methanol, and evaporation of the methanol followed by dissolution in 15 mL of water. After addition of $NaClO_4$ (2 g), the product crystallized as pale blue needles very similar in color to those of $Cu(SO_4) \cdot 5H_2O$. A quantity of the product was recrystallized from hot water to yield X-ray-quality crystals. UV–visible (aqueous solution): λ_{max} 603 nm, ϵ 217 dm^3·mol^{-1}·cm^{-1}. IR (KBr pellet): 1550, 1380, 1350 cm^{-1}. Anal. Calcd for $C_{15}H_{31}Cl_2CuN_5O_6$: C, 35.20; H, 6.10; N, 13.68. Found: C, 34.72; H, 6.12; N, 13.46.

X-ray Crystallographic Studies. The data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å). The cell dimensions were obtained from least-squares refinement of 25 high-θ reflections. An ω–2θ scan mode was used with a scan width of $(0.6 + 0.35 \tan \theta)^\circ$ and a variable scan speed. Three standard reflections were monitored and showed no significant variation over the data collection. Lp and absorption corrections were applied to the data according to the method of North et al.[16] An estimate of agreement between equivalent reflections was not made. Six reflections were checked for monoclinic equivalences ($hk\bar{l}$, $h\bar{k}l$, $\bar{h}\bar{k}\bar{l}$, and $\bar{h}k\bar{l}$). Crystal data and data collection parameters are given in Table I.

Table I. Crystallographic Data for [Cu(NE-3,3-HP)Cl]ClO$_4$

formula	$C_{15}H_{31}CuN_5O_6Cl_2$
fw	511.86
space group	monoclinic, $P2_1/n$ (No. 14), unique axis *b*, cell choice 2
a, Å	6.709 (1)
b, Å	29.610 (2)
c, Å	10.653 (1)
β, deg	97.398 (8)
V, Å^3	2098.75
Z	4
D_c	1.62
D_m	1.62
T, °C	25
$\lambda_{Mo\ K\alpha}$, Å	0.71073
abs coeff, cm^{-1}	12.66
transm coeff	92.73–99.96
R_w[a]	0.0436
final R[b]	0.0412

[a] $R_w = (\sum w\Delta F^2/\sum wF_o^2)^{0.5}$; $w = 1.8092/(\sigma^2(F) + 0.000819F^2)$. [b] $R = \sum \Delta F/\sum F_o$.

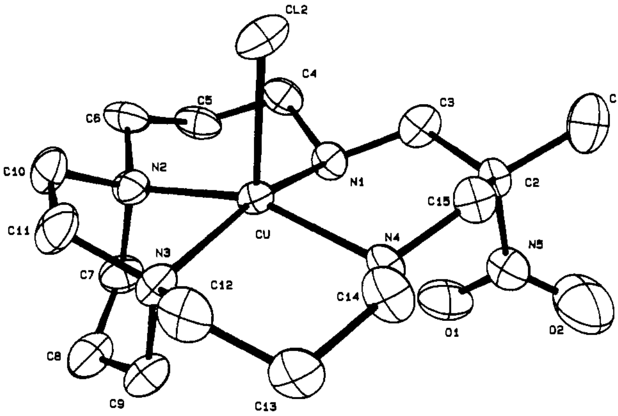

Figure 3. ORTEP[18] drawing of the complex cation in [Cu(NE-3,3-HP)-Cl]ClO$_4$ with 50% probability thermal ellipsoids, showing the numbering scheme.

The structure was solved and refined by using the Patterson and Fourier techniques of the programs SHELXS-86 and SHELX76,[17] respectively. The scattering factors and anomalous dispersion corrections for Cu(II) were obtained from ref 22, while the values for the other atoms were taken from the program SHELX76. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at geometrically calculated positions with constrained bond lengths of 1.08 Å. Isotropic thermal parameters for the hydrogens were tied to a single free variable, which refined to 0.05428 Å^2. In the final stages of refinement, a weighted full-matrix least-squares analysis with a weighting scheme $w = 1.8092/(\sigma^2(F) + 0.000819F^2)$ was used. Corrections for extinction were not made during the refinement.

Fractional atomic coordinates for the structure are given in Table II, and a selection of bond lengths and angles is given in Table III.

Spectroscopy. The electronic spectrum of the Cu(II) complex of Ne-3,3-HP was recorded in aqueous solution on a Cary 2300 spectrophotometer.

Results and Discussion

An ORTEP[18] drawing of the complex cation $[Cu(NE\text{-}3,3\text{-}HP)Cl]^+$ is seen in Figure 3. The coordination geometry around

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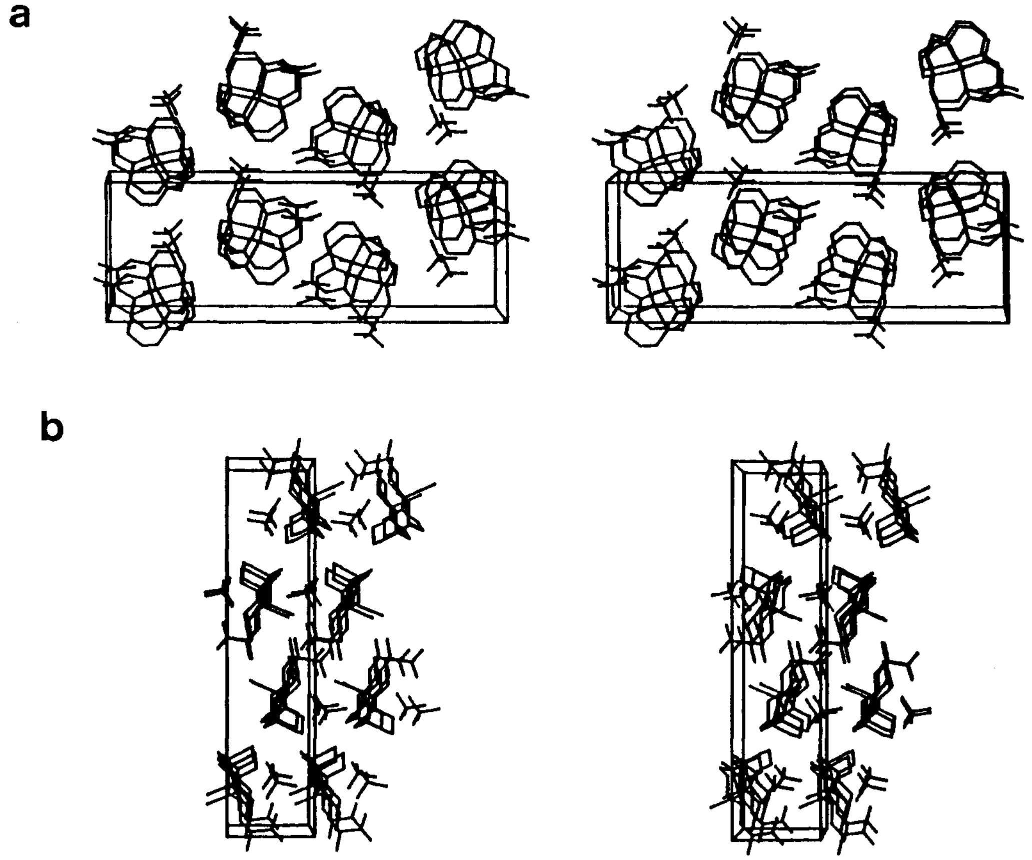

Figure 4. Stereoview (PLUTO[23]) of four unit cells of the complex [Cu(NE-3,3-HP)Cl]ClO_4 as viewed down (a) the *a* axis and (b) the *c* axis of the unit cell.

Table II. Fractional Coordinates (×10^4; Cu and Cl, ×10^5) and Equivalent Isotropic Temperature Factors (Å^2 × 10^3; Cu and Cl, ×10^4) for [Cu(NE-3,3-HP)Cl](ClO_4)

	x/*a*	*y*/*b*	*z*/*c*	U_{eq}[a]
Cu	10228 (7)	12060 (2)	13412 (4)	257 (1)
C(1)	2212 (8)	−266 (2)	3358 (5)	53 (1)
C(2)	2660 (7)	214 (2)	2925 (4)	36 (1)
C(3)	1423 (7)	548 (2)	3589 (4)	37 (1)
N(1)	1499 (5)	1033 (1)	3267 (3)	31 (1)
HN(1)	3029 (5)	1148 (1)	3498 (3)	54 (3)[b]
C(4)	85 (7)	1250 (2)	4070 (4)	40 (1)
C(5)	126 (7)	1758 (2)	4056 (5)	44 (1)
C(6)	−864 (7)	1948 (2)	2835 (5)	44 (1)
N(2)	292 (5)	1869 (1)	1753 (3)	34 (1)
C(7)	2228 (7)	2119 (2)	1980 (5)	41 (1)
C(8)	3170 (7)	2206 (2)	776 (5)	48 (1)
C(9)	3354 (6)	1795 (2)	−34 (5)	39 (1)
C(10)	−983 (7)	2042 (2)	590 (5)	43 (1)
C(11)	−281 (7)	1866 (2)	−617 (5)	44 (1)
N(3)	1411 (5)	1545 (1)	−335 (3)	32 (1)
C(12)	1457 (7)	1273 (2)	−1505 (4)	42 (1)
C(13)	3027 (7)	907 (2)	−1372 (4)	39 (1)
C(14)	2516 (8)	534 (2)	−511 (4)	40 (1)
N(4)	2728 (5)	655 (1)	862 (3)	27 (1)
HN(4)	4240 (5)	771 (1)	1167 (3)	54 (3)[b]
C(15)	2266 (7)	228 (2)	1494 (4)	33 (1)
N(5)	4909 (6)	304 (1)	3297 (3)	39 (1)
O(1)	5444 (5)	682 (2)	3522 (4)	64 (1)
O(2)	6069 (7)	−5 (2)	3298 (6)	98 (1)
Cl(2)	−22758 (15)	8645 (4)	7792 (12)	438 (3)
Cl(1)	54335 (17)	15732 (4)	59508 (10)	403 (3)
O(11)	5378 (5)	1774 (1)	4729 (3)	61 (1)
O(12)	4282 (7)	1173 (1)	5863 (4)	71 (1)
O(13)	7450 (6)	1472 (2)	6429 (4)	102 (2)
O(14)	4595 (9)	1871 (2)	6766 (5)	99 (2)

[a] $U_{eq} = {}^{1}/_{3}\sum_i\sum_j U_{ij}a^*_i a^*_j(\mathbf{a}_i\cdot\mathbf{a}_j)$. [b] Isotropic temperature factor.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for [Cu(NE-3,3-HP)Cl]ClO_4 ($C_{15}H_{31}Cl_2CuN_5O_6$)

Cu–N(1)	2.098 (3)	Cu–N(2)	2.083 (3)	Cu–N(3)	2.094 (4)
Cu–N(4)	2.094 (3)	Cu–Cl(2)	2.437 (1)	C(2)–C(15)	1.513 (6)
C(3)–N(1)	1.479 (6)	N(5)–O(1)	1.192 (5)	C(2)–N(5)	1.533 (6)
C(4)–N(1)	1.501 (5)	C(8)–C(9)	1.503 (7)	Cl(1)–O(11)	1.427 (3)

N(1)–Cu–N(2)	92.0 (1)	N(1)–Cu–N(3)	158.5 (1)
N(1)–Cu–N(4)	91.7 (1)	N(2)–Cu–N(3)	77.7 (1)
N(2)–Cu–N(4)	159.5 (1)	N(3)–Cu–N(4)	92.0 (1)
N(1)–Cu–Cl(2)	99.1 (1)	N(1)–Cu–Cl(2)	102.2 (1)
N(3)–Cu–Cl(2)	101.4 (1)	N(4)–Cu–Cl(2)	97.1 (1)
Cu–N(1)–C(3)	117.3 (3)	Cu–N(1)–C(4)	115.2 (3)
Cu–N(2)–C(6)	118.2 (3)	Cu–N(2)–C(7)	106.2 (3)
Cu–N(2)–C(10)	105.8 (3)	Cu–N(3)–C(9)	104.7 (3)
Cu–N(3)–C(11)	107.7 (3)	Cu–N(3)–C(12)	118.2 (3)
Cu–N(4)–C(14)	116.0 (3)	Cu–N(4)–C(15)	113.6 (2)
O(1)–N(5)–(2)	122.5 (5)	C(2)–N(5)–O(1)	118.4 (4)

Table IV. Least-Squares Plane[a] of Nitrogen Donors

atom	dev from plane, Å	atom	dev from plane, Å
N(1)	0.0091	N(4)	−0.0091
N(2)	−0.0104	Cu	−0.3585
N(3)	0.0104		

[a] Equation of plane in fractional coordinates: $5.9997x + 10.9913y + 1.4138z = 2.4873$.

the Cu(II) is essentially square pyramidal, with a chloride occupying the axial coordination site. A stereoview of the unit cell (Figure 4a) shows that the complex cations are stacked in columns, as are also the perchlorate anions. The stacking of the complex cations leads to the possibility of the axial chloride forming a Cu–Cl–Cu bridge between adjacent complex cations in the stack. However, a side view of the stack (Figure 4b) shows that the axial chloride and the copper to which it is coordinated are not collinear with a neighboring copper in the stack, and the Cu- -Cl distance for adjacent complex cations is quite long at 4.72 Å. The mean

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(23) Motherwell, W. D. S. PLUTO structure plotting program. University of Cambridge, England, 1989.

bond length for this reinforced macrocyclic complex is much longer at 2.09 Å than any of the unreinforced analogues, as seen in Figure 2. This supports the idea that the reinforcement of a large macrocyclic ring can lead to considerable bond stretching ability. What is striking, and rather unexpected, about the complex is the fact that the Cu(II) lies considerably out of the plane of the nitrogen donors, being some 0.36 Å out of the plane (Table IV). This is surprising in view of the fact that the Cu-N bond is being stretched, which can only be increased by the fact of the Cu(II) lying out of the plane. At this stage one must conjecture that this effect might be a result of the steric requirements of coordination to the homopiperazine part of the macrocycle.

One of the striking properties of the tetraazamacrocycles is the very high ligand field (LF) strength that is found in some of the complexes, seen for the Cu(II) complex of 2,3,2-NE in Figure 2. This was first interpreted by Busch et al.[13] as arising from compression of the metal ion in the too-small cavity of the macrocyclic ligand. This is a reasonable interpretation, except that the cases where the LF is highest correspond to the situation where the metal ion fits best into the cavity of the macrocycle, rather than where the metal ion is too large. This observation fits very nicely the set of complexes in Figure 2, where it is seen that the short Cu-N bonds in the 2,2,2-NE complex do not produce a higher LF strength. We have suggested on many occasions[4,5,19-21] that the higher LF strength is derived from the higher donor strength of the nitrogens as one moves along the series zeroth (ammonia) < primary < secondary < tertiary. The factors governing LF strength depend on the amount of overlap in the M-N bond, which is controlled by (1) the nature of the nitrogen donors in the series primary < secondary < tertiary, (2) the extent of stretching of the M-N bond away from the ideal value, and (3) N-M-N bond angle distortion, which appears to lower overlap strongly in the M-N bond and hence lessen LF strength. This last contribution will be discussed more fully in a future paper. At this stage, it appears that N-M-N bond angle deformation involving the in-plane N-M-N angles and also N-M-N bond angle deformation due to the metal ion rising out of the plane of the donor atoms contribute to a lowering of the LF strength. With respect to factor 2, no doubt bond compression should raise the LF strength, but metal ions appear to escape compression by N-M-N bond angle deformation to lie outside of the plane of the donor atoms, which leads to an overall lowering of LF strength due to factor 3, which is bond angle deformation.

One thus sees in Figure 2 that the LF strength of the complex $[Cu(NE\text{-}3,3\text{-}HP)]^{2+}$ is exceedingly low and is higher only than that of the 3,3,3-NE complex. One might say from the contribution from factor 1 above, the donor strength of the nitrogens, that the LF strength of the NE-3,3-HP complex should be exceedingly high, with its two tertiary nitrogens as compared to all secondary nitrogens in the unbridged analogues, but the very great extent of bond stretching and N-Cu-N bond angle deformation overwhelm this contribution. The effect of the tertiary nitrogens is apparent however, in that the LF strength in the NE-3,3-HP complex is actually higher than that in the 3,3,3-NE complex, in spite of the much lower extent of Cu-N bond stretching and N-Cu-N bond angle deformation in the 3,3,3-NE than in the NE-3,3-HP complex. That the tertiary nitrogens present in reinforced macrocycles can lead to high LF strengths is seen[11] in that the low-spin Ni(II) complex of AM-2,2-HP has the highest LF strength reported for any complex of this ion with a tetradentate saturated nitrogen donor ligand.

The structure of the $[Cu(NE\text{-}3,3\text{-}HP)Cl]ClO_4$ complex has demonstrated how much more strongly M-N bonds may be stretched in the cavities of reinforced macrocycles than in their unreinforced analogues. Previous work has shown[8] how strongly the reinforced macrocycles can compress metal ions. We are currently attempting the synthesis of the NE-3,3-DAC complex of Cu(II) to see how more strongly this might stretch the Cu-N bond.

Acknowledgment. We thank the Foundation for Research Development and the University of the Witwatersrand for generous support for this work.

Supplementary Material Available: Tables of fractional coordinates, anisotropic temperature factors, complete bond angles and lengths, and details of the crystallographic analysis for $[Cu(NE\text{-}3,3\text{-}HP)Cl]ClO_4$ and a stereoview of the complex (9 pages); a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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Are Internal Flips of M-M Multiple Bonds within Cubic or Octahedral Ligand Fields Symmetry Allowed?

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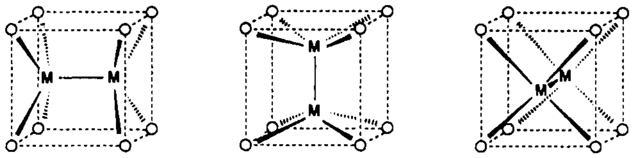
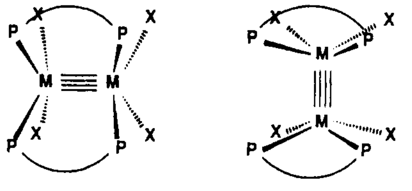
Many dinuclear complexes of the general formula M_2X_8 that contain a M-M quadruple bond exhibit a nearly cubic arrangement of the ligands X. Often complexes of this type display a crystallographic disorder of the M_2 vector among the three possible M-M orientations within the cube defined by the eight ligands; see I.[1-5] Upon lowering of the symmetry of the M_2X_8 system by ligand substitution, compounds such as $M_2X_4(L\frown L)_2$ have been prepared and shown to adopt both α and β isomeric forms (II).[6-10]



I



II

Cotton and co-workers have studied the isomerization of α and β isomers of complexes of type II and provided evidence that this process, which occurs even in the solid state, proceeds via an "internal flip" of the M_2 vector.[11-14] More recently in the study of M_2X_6 triple-bonded compounds, there have been examples of disordering of M_2 units within an octahedral ligand arrangement. For example, in the X-ray crystal structure of $W_2(OSi(t\text{-}Bu)Me_2)_6$, the W-W axis was found to be disordered over three of the four

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