temperature, a result of depopulating the higher energy well; this is consistent with the experimental results and strongly implies that the cis-octahedral CuN_4O_2 chromophore is fluxional. The fact that the $\delta°$ values of **1** are greater than those of **2**, a d^{10} complex whose crystal is isostructural, indicates that the "driving force" governing the distortional behavior is vibronic in origin and is not related to crystal-packing forces etc. (Cooperative forces in **1** are also unimportant: the electronic reflectance and ESR spectra for Cu(II)-doped **2** show no discernible variations from 0.1–100% copper doping.[5]) The derivation presented allows ΔE to be easily determined from X-ray diffraction experiments performed at different temperatures, and it seemingly repudiates the notion that "X-ray analysis thus provides information about the preferred conformations of molecules although it has nothing to say about the energy differences between the conformations or the energy barriers that separate them. This information has to be obtained by other methods."[23]

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Registry No. 1, 23578-78-1.

Supplementary Material Available: Tables of final positional and thermal parameters (Tables S1 and S2), bond distances and angles (Tables S3 and S4), and observed and calculated structure factors (Tables S5 and S6) (32 pages). Ordering information is given on any current masthead page.

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Contribution from the Institute for Inorganic Chemistry,
University of Göttingen, Göttingen, West Germany,
and the Department of Chemistry, Manchester University,
Manchester M13 9PL, U.K.

Steric and Crystal-Packing Effects on the Molecular Structures of Dimetal(II) Tetrakis(2-oxypyridine) Complexes

William Clegg,*[1a] C. David Garner,*[1b] Lalarukah Akhter,[1b]
and M. Hassan Al-Samman[1b]

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The anions of 6-methyl-2-hydroxypyridine (Hmhp) and 6-chloro-2-hydroxypyridine (Hchp) form bridged binuclear complexes of the type $M_2(mhp)_4$[2-5] and $M_2(chp)_4$[6,7] with a number of transition metals. Across the series $[Mo_2(mhp)_4]\cdot CH_2Cl_2$,[2] $[Ru_2(mhp)_4]\cdot CH_2Cl_2$,[3] and $[Rh_2(mhp)_4]$,[4] crystal structure determinations have demonstrated a progression toward longer M–M and shorter M–O and M–N bonds. $[Pd_2(mhp)_4]$[5] differs markedly from the Rh dimer only in the M–M separation and angles that depend directly on it. In parallel with this progression is an increase in the mean O–M–M–N torsion angle away from an exactly eclipsed conformation, in the order Mo < Ru < Rh ≈ Pd. We have interpreted this as a direct consequence of intramolecular steric repulsions between methyl groups of the ligands.[3,4] We were, therefore, surprised to see a report of the structure of $[Rh_2(mhp)_4]\cdot H_2O$,[7] in which two crystallographically independent molecules have mean torsion angles of 1.0 and 9.3°, which are respectively lower and higher than any previously observed for $M_2(mhp)_4$ complexes. Furthermore, the mean Rh–Rh bond length of 2.367 (1) Å was interpreted as significantly longer than the 2.359 (1) Å observed in anhydrous $Rh_2(mhp)_4$.[4] This structure raises the question of the effect of crystal-packing forces (the ultimate appeal of crystallographers in search of explanations!) on the molecular structures and, in particular, on the M–M bond lengths and torsional distortions about the M–M bonds in these dimers.

Table I. Crystal Data[a]

	1	**2**	**3**
formula	$C_{24}H_{24}N_4O_4Mo_2$	$C_{24}H_{24}N_4O_4Mo_2\cdot CH_3OH$	$C_{24}H_{24}N_4O_4Rh_2\cdot CH_2Cl_2$
cryst color and habit	yellow laths	orange blocks	yellow blocks
fw	624.4	656.4	723.2
cryst size, mm	0.35 × 0.23 × 0.15	0.25 × 0.12 × 0.19	0.19 × 0.35 × 0.50
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a, Å	8.865 (1)	8.938 (1)	12.705 (1)
b, Å	10.724 (1)	11.043 (2)	17.240 (1)
c, Å	13.750 (1)	13.903 (2)	12.769 (1)
α, deg	85.69 (1)	94.30 (2)	90
β, deg	77.98 (1)	95.98 (2)	103.58 (1)
γ, deg	77.36 (1)	103.87 (2)	90
V, Å^3	1246.9	1317.9	2718.7
d_{calcd}, g cm^{-3}	1.663	1.654	1.767
Z	2	2	4
μ, cm^{-1}	10.17	9.69	14.31
transmissn factor	[b]	0.746–0.819[c]	0.526–0.613[c]
$2\theta_{max}$, deg	50	55	55
no. of data collcd	4597	6101	6500
no. of data $F > 4\sigma(F)$	2686	3591	5447
no. of refined parameters	319	337	346
g[d]	0.0003	0.0005	0.0005
R[e]	0.028	0.063	0.046
R_w[f]	0.039	0.060	0.062
variance,[g] e	0.98	2.26	1.73
slope[h]	1.34	1.13	1.82
largest peak,[i] e Å^{-3}	0.35	0.81	0.96

[a] Valid for all three data sets: Stoe-Siemens AED diffractometer, Mo Kα radiation, $\lambda = 0.71069$ Å, graphite monochromator; all measurements at room temperature. [b] No absorption corrections. [c] Semiempirical absorption corrections based on intensities measured at various azimuthal angles. [d] Weighting scheme: $w^{-1} = \sigma^2(F) + gF^2$. [e] $R = \Sigma|\Delta|/\Sigma|F_o|$; $\Delta = |F_o| - |F_c|$. [f] $R_w = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$. [g] Variance $= (\Sigma w\Delta^2/\Sigma w)^{1/2}$. [h] Slope of normal probability plot. [i] In final difference synthesis.

In the course of our studies of complexes of mhp, we have obtained crystals of two further forms of $Mo_2(mhp)_4$, one as a methanol solvate and the other with no solvent of crystallization. We report here the structures of these and of $[Rh_2(mhp)_4]\cdot CH_2Cl_2$.

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Table II. Atomic Coordinates ($\times 10^4$)

	1			**2**			3		
atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
M(1)	3904 (1)	1787 (1)	2802 (1)	3582 (1)	1297 (1)	3523 (1)	1779 (1)	1742 (1)	2729 (1)
M(2)	3042 (1)	3729 (1)	2643 (1)	3818 (1)	1792 (1)	2130 (1)	2463 (1)	498 (1)	3311 (1)
O(1)	1606 (3)	3912 (2)	4051 (2)	5340 (6)	3551 (5)	2575 (3)	2820 (2)	867 (1)	4861 (2)
C(11)	1555 (5)	2905 (4)	4632 (3)	5820 (8)	3851 (7)	3499 (5)	2679 (3)	1583 (2)	5087 (3)
C(12)	563 (6)	2954 (4)	5574 (3)	6950 (9)	4965 (8)	3835 (6)	2975 (3)	1835 (2)	6168 (3)
C(13)	560 (6)	1873 (5)	6149 (4)	7430 (9)	5254 (8)	4809 (6)	2857 (5)	2593 (3)	6412 (4)
C(14)	1549 (7)	708 (5)	5810 (3)	6804 (10)	4442 (8)	5448 (6)	2425 (5)	3114 (3)	5595 (4)
C(15)	2482 (6)	690 (4)	4876 (3)	5698 (9)	3362 (8)	5114 (6)	2137 (4)	2866 (2)	4554 (4)
C(16)	3510 (7)	−503 (4)	4434 (4)	4918 (12)	2444 (9)	5755 (6)	1672 (5)	3382 (3)	3615 (4)
N(1)	2514 (4)	1777 (3)	4292 (2)	5202 (7)	3063 (6)	4142 (4)	2269 (3)	2099 (2)	4307 (3)
O(2)	5862 (3)	1965 (2)	3341 (2)	5443 (6)	470 (5)	3612 (3)	318 (2)	1445 (2)	2971 (2)
C(21)	6079 (5)	3103 (4)	3477 (3)	6195 (9)	425 (7)	2863 (5)	134 (3)	742 (2)	3241 (3)
C(22)	7345 (5)	3278 (4)	3857 (3)	7415 (10)	−189 (8)	2861 (7)	−897 (3)	537 (3)	3344 (4)
C(23)	7495 (6)	4477 (5)	4009 (3)	8132 (10)	−238 (9)	2042 (7)	−1103 (4)	−208 (3)	3660 (4)
C(24)	6369 (6)	5528 (5)	3787 (4)	7694 (9)	333 (8)	1239 (7)	−261 (4)	−756 (3)	3842 (4)
C(25)	5159 (5)	5329 (4)	3396 (3)	6535 (9)	952 (8)	1265 (5)	741 (3)	−537 (2)	3737 (3)
C(26)	3908 (6)	6404 (4)	3129 (4)	6021 (10)	1600 (9)	449 (6)	1675 (4)	−1088 (3)	3925 (4)
N(2)	4977 (4)	4124 (3)	3236 (2)	5790 (7)	971 (6)	2075 (4)	938 (2)	197 (2)	3438 (2)
O(3)	4229 (3)	3896 (3)	1185 (2)	2459 (6)	109 (5)	1423 (4)	2108 (2)	109 (2)	1788 (2)
C(31)	5058 (5)	2871 (4)	738 (3)	1889 (8)	−779 (8)	1932 (5)	1584 (4)	552 (2)	1015 (3)
C(32)	5789 (6)	2899 (5)	−272 (3)	1064 (10)	−1963 (8)	1510 (7)	1261 (4)	236 (3)	−46 (3)
C(33)	6670 (6)	1815 (5)	−701 (4)	448 (11)	−2860 (9)	2066 (7)	685 (5)	686 (3)	−833 (4)
C(34)	6868 (6)	672 (5)	−139 (4)	605 (10)	−2591 (8)	3072 (7)	415 (5)	1452 (3)	−639 (4)
C(35)	6148 (6)	654 (4)	845 (3)	1404 (9)	−1416 (8)	3495 (6)	762 (4)	1739 (3)	378 (4)
C(36)	6312 (7)	−506 (5)	1509 (4)	1604 (11)	−1020 (9)	4560 (6)	562 (5)	2559 (3)	658 (4)
N(3)	5216 (4)	1751 (3)	1279 (3)	2079 (7)	−517 (6)	2923 (4)	1339 (3)	1292 (2)	1203 (3)
O(4)	2113 (4)	1227 (3)	2295 (2)	1667 (6)	2022 (5)	3679 (4)	3234 (2)	2059 (2)	2478 (2)
C(41)	1056 (5)	2097 (5)	1972 (3)	1106 (8)	2537 (7)	2965 (5)	4040 (3)	1588 (2)	2715 (3)
C(42)	−116 (6)	1766 (6)	1559 (4)	−185 (9)	3038 (7)	3002 (6)	5075 (4)	1824 (3)	2576 (4)
C(43)	−1170 (7)	2715 (6)	1193 (4)	−716 (9)	3575 (8)	2233 (7)	5928 (4)	1334 (3)	2857 (4)
C(44)	−1080 (6)	3990 (6)	1225 (4)	33 (9)	3635 (8)	1391 (7)	5798 (4)	606 (3)	3272 (4)
C(45)	61 (6)	4278 (5)	1644 (3)	1278 (9)	3148 (8)	1364 (6)	4800 (3)	383 (2)	3381 (3)
C(46)	242 (7)	5617 (5)	1714 (4)	2173 (11)	3141 (10)	514 (6)	4584 (4)	−408 (2)	3744 (4)
N(4)	1125 (4)	3353 (4)	2026 (2)	1839 (7)	2595 (6)	2138 (5)	3943 (2)	873 (2)	3125 (2)
O(5)				3754 (12)	4656 (10)	8669 (6)			
C(5)				4714 (24)	3735 (14)	8581 (11)			
C(50)							3793 (11)	1222 (9)	9823 (7)
Cl(1)							4118 (2)	2181 (2)	9408 (2)
Cl(2)							3868 (3)	533 (1)	8918 (2)

Table III. Structural Features of $M_2(mhp)_4 \cdot L$ and $M_2(chp)_4$ Complexes

$M_2(mhp)_4 \cdot L$

	M										
	Mo	Mo	Mo	Ru	Rh	Rh	Rh	Rh	Pd	Cr	W
L	CH_2Cl_2		MeOH	CH_2Cl_2		CH_2Cl_2	H_2O	H_2O		CH_2Cl_2	CH_2Cl_2
M-M, Å	2.065 (1)	2.067 (1)	2.068 (1)	2.238 (1)	2.359 (1)	2.367 (1)	2.370 (1)	2.365 (1)	2.546 (1)	1.889 (1)	2.161 (1)
mean *d*(M-N), Å	2.167 (14)	2.171 (7)	2.174 (10)	2.089 (5)	2.043 (5)	2.053 (5)	2.045 (8)	2.037 (8)	2.046 (16)	2.067 (4)	2.11 (3)
mean *d*(M-O), Å	2.086 (7)	2.077 (4)	2.081 (9)	2.044 (10)	2.017 (4)	2.019 (9)	2.021 (6)	2.017 (5)	2.013 (8)	1.969 (9)	2.037 (7)
mean *d*(M-N) − mean *d*(M-O), Å	0.081 (16)	0.094 (9)	0.093 (12)	0.045 (12)	0.026 (5)	0.034 (10)	0.024 (9)	0.020 (9)	0.033 (18)	0.098 (10)	0.07 (3)
mean N-M-M-O torsion, deg	1.3 (4)	1.4 (9)	0.8 (6)	3.5 (6)	6.1 (9)	3.7 (5)	1.0 (8)	9.3 (6)	6.4 (12)	1.9 (3)	1.4 (8)
ref	2			3	4		7	7	5	2	2

$M_2(chp)_4$

	M					M			
	Cr	W	Mo	Rh		Cr	W	Mo	Rh
M-M, Å	1.955 (2)	2.177 (1)	2.085 (1)	2.379 (1)	mean *d*(M-N) − mean *d*(M-O), Å	0.082 (13)	0.05 (4)	0.064 (13)	0.039 (24)
mean *d*(M-N), Å	2.060 (10)	2.12 (3)	2.153 (11)	2.050 (19)	mean N-M-M-O torsion, deg	4.3 (12)	3.0 (13)	3.1 (10)	4.8 (12)
mean *d*(M-O), Å	1.978 (11)	2.07 (1)	2.089 (9)	2.011 (12)	ref	6	6	6	7

Experimental Section

$Mo_2(mhp)_4$ (**1**) was obtained as crystals directly from the reaction of Hmhp with $Mo(CO)_6$ in diglyme (18 h at room temperature under purified dinitrogen), analogous to the original preparation of $W_2(mhp)_4$.[2] Recrystallization of this from methanol gave crystals of $[Mo_2(mhp)_4]\cdot MeOH$ (**2**).

$[Rh_2(mhp)_4]\cdot CH_2Cl_2$ (**3**) was obtained by recrystallization of $Rh_2(mhp)_4$[4] from CH_2Cl_2.[7] Crystals of each complex were sealed in Lindemann glass capillaries for X-ray investigation. The methods used for data collection and structure determination have been described elsewhere.[5] All three structures were refined with anisotropic thermal parameters and with hydrogen atom constraints.[8] Crystal

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(8) Computer programs were written by G. M. Sheldrick (SHELXTL system; Göttingen) and W. Clegg (diffractometer control program) for Data General Eclipse and Nova computers.

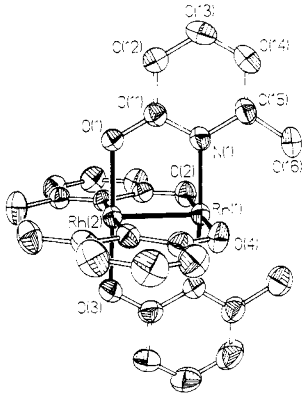

Figure 1. Molecular structure of $Rh_2(mhp)_4$ in **3**. Thermal motion is shown as 50% probability ellipsoids.

data are summarized in Table I. Atomic coordinates are given in Table II. Table III compares the essential results with those of previously determined $M_2(mhp)_4$ and $M_2(chp)_4$ structures. Detailed results, together with structure factor tables, are available as supplementary material.

Results and Discussion

The molecular structure of **3** is depicted in Figure 1; the atom-numbering scheme is the same as in all our studies of $M_2(mhp)_4$ structures. The structure is essentially the same as for **1**, **2**, and the other related dimers.

The molecular structure of $Mo_2(mhp)_4$ varies insignificantly with crystal packing in all three crystal structures; no significant differences are observed in the bond lengths or even in the conformational twist about the Mo–Mo bond. It might be expected that the eclipsed conformation of a quadruple bond, which contains a δ component, would be particularly insensitive to factors favoring a twisting distortion, but torsion angles of up to 30° have been observed, whereby the δ component has been estimated to lose only approximately 50% of its contribution to the Mo–Mo bonding.[9]

The single Rh–Rh bond shows a greater variation of twist, reflecting its inherently weaker nature and the σ symmetry of the net Rh–Rh bond. The range of observed Rh–Rh bond lengths in these $Rh_2(mhp)_4$ structures is, however, very small, and the differences observed are of dubious significance in the absence of special precautions in the determination of unit cell parameters.

When all the crystallographic results now available for molecules of this type are considered together, it appears that the torsional conformation of the $M_2(mhp)_4$ and $M_2(chp)_4$ molecules is determined by a balance of several factors, which are given as follows, in decreasing order of importance.

(1) Bonding Characteristics of the M_2 Unit Bridged by Four Ligands of the mhp Type. The preference here is always for an eclipsed conformation, with that for the Mo–Mo quadruple bond being significantly more marked than that for the Rh–Rh single bond.

(2) Intramolecular Steric Interactions between the Ligands, Notably the Me···Me or Cl···Cl Interactions of Mutually Trans Ligands. A twist away from the eclipsed conformation relieves this repulsion. We have already discussed this effect for $M_2(mhp)_4$ complexes[3,4] and note that the known $M_2(chp)_4$ structures also fit into this pattern (Table III). These $M_2(chp)_4$ complexes (and $Rh_2(mhp)_4$) are all isostructural (space group *Pbca*), so variations in packing forces are slight. The relatively small increase in mean torsion angle in moving from $Mo_2(chp)_4$ to $Rh_2(chp)_4$, compared with the rather larger difference for the corresponding mhp complexes, mirrors the smaller variation in [mean d(M–N) – mean d(M–O)] for the chp complexes; i.e., the intramolecular steric repulsion effect shows much less variation for the chp complexes. Moreover, in both groups of complexes $M_2(mhp)_4$ and $M_2(chp)_4$ with M = Cr, Mo, or W,[2,6] the largest degree of twisting distortion is for M = Cr; here steric interaction will be at its greatest for each triad, because of the shorter Cr–N bonds. Although these torsion angles, and differences between them, are small, a satisfactory and convincing overall pattern does emerge from the complete set of known structures. Extreme steric effects, with twists of around 20°, are observed when four mhp or chp ligands are arranged about a Rh_2 unit, such that three methyl groups or chlorine atoms lie at one end of the molecule.[7,10]

(3) Intermolecular Interactions between Molecules and with Solvent Molecules. For normal van der Waals interactions (when the solvent of crystallization is methanol, CH_2Cl_2, or nonexistent), the effect is a minor one, overlaid on factors 1 and 2. In the case of $[Rh_2(mhp)_4]\cdot H_2O$, however, the rather stronger hydrogen bonds[7] have a much greater effect on the torsional conformation of the dimeric molecule.

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Supplementary Material Available: Listings of bond lengths and angles, thermal parameters, atomic coordinates, and structure factors (80 pages). Ordering information is given on any current masthead page.

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Contribution from the Chemical Technology Division,
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

X-ray Diffraction and Thermal Analysis of Molybdenum(VI) Oxide Hemihydrate: Monoclinic $MoO_3\cdot{}^1/_2H_2O$[1]

R. L. Fellows,*[2] M. H. Lloyd,[2] J. F. Knight,[3] and H. L. Yakel[4]

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Molybdenum(VI) oxide is known to form a rich family of crystalline hydrates that include a monoclinic dihydrate, $MoO_3\cdot 2H_2O$,[5] two monohydrates, the yellow monoclinic $MoO_3\cdot H_2O$[6] and the white triclinic $MoO_3\cdot H_2O$,[7] and a white hemihydrate.[8] A molybdenum oxide hemihydrate phase has

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(2) Chemical Technology Division.

(3) Current address: Oak Ridge Gaseous Diffusion Plant, Separations Systems Division.

(4) Metals and Ceramics Division.

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