Structures of $[M_2(dimen)_4](Y)_2$ (M = Rh, Ir; dimen = 1,8-Diisocyanomenthane; Y = PF_6, Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, $B(C_6H_5)_4$) Crystals Featuring an Exceptionally Wide Range of Metal−Metal Distances and Dihedral Twist Angles

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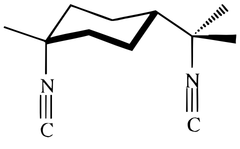
Received July 7, 1995

Previous reports of "bond-stretch" isomerism in mononuclear transition metal complexes have been critically reexamined[1,2] because of misinterpretation of structural or compositional disorder; however, the viability of this type of isomerism in spin-crossover systems has recently been discussed.[3] Bond-stretch isomerism in compounds with metal−metal bonds has also been proposed: in addition to the evidence that two bond-stretch isomers of the Cr_2 molecule exist in the gas-phase,[4] a related type of isomerism ("deformational isomerism")[5] has been reported for $[Cp^*RuCl_2]_2$ ($Cp^* = \eta^5$-C_5Me_5)[5] and $[Rh_2(\mu\text{-}Cl)_2(CNC_8H_9)_4(\mu\text{-}AuP(C_6H_5)_3]_2(PF_6)_2$.[6] Deformational isomerism occurs when two or more molecular forms differ only in M−M distance and a coupled ligand deformation coordinate (*i.e.*, an L−M−L angle and/or an L−M−M−L dihedral angle).

A wide range of M−M distances (2.72−5.28 Å) and L−M−M−L dihedral twist angles (ω = 0−39°) has been observed for binuclear dimen (1,8-diisocyanomenthane) complexes.[2,7]



dimen (1,8-diisocyanomenthane)

Pertinent structural data from five X-ray crystal structures[8] in the $[M_2(dimen)_4](Y)_2$ series (M = Rh, Ir; Y = PF_6, TFPB (TFPB = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate),[9] and $B(C_6H_5)_4$)[2,10−12] are illustrated in Figure 1. In each case, the M−M distances for the $Ir_2(dimen)_4{}^{2+}$ salts are shorter than those for the corresponding $Rh_2(dimen)_4{}^{2+}$ salts.[13] Interestingly, the Rh(I) ($d(Rh_2) = 3.262$)[14] and Ir(I) ($d(Ir_2) = 3.119$ Å)[13b] complexes of TM4 (TM4 = 2,5-diisocyano-2,5-dimethylhexane) show a similar trend.

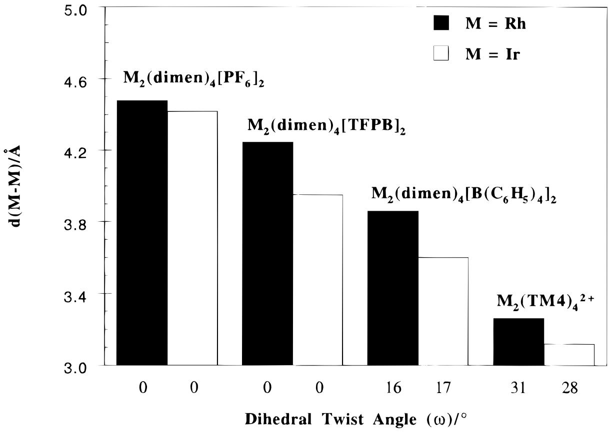


Figure 1. Selected M−M distances and average C−M−M−C dihedral twist angles from $[M_2(L)_4](Y)_2$ crystal structures. The first three pairs of bars are for $[M_2(dimen)_4](Y)_2$; the fourth pair of bars is for $[M_2(TM4)_4](Y)_2$. $[Rh_2(dimen)_4](PF_6)_2$ data are from ref 8; $[M_2(TM4)_4](Y)_2$ data are from refs 13b and 14.

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(11) The X-ray data were collected on Enraf-Nonius SDP-CAD-4 diffractometers with graphite monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å). Data for the $PF_6{}^-$ and $TFPB^-$ salts were collected in the *hkl* octant. Data for the $B(C_6H_5)_4{}^-$ salts were collected in the *hkl*, $\bar{h}kl$, $h\bar{k}l$, and $hk\bar{l}$ octants. All structures (except M = Rh, Y = $B(C_6H_5)_4$) were solved by direct methods using PHASE, DIRDIF, and TEXSAN software. The structure of $[Rh_2(dimen)_4][B(C_6H_5)_4]_2$ was solved from a Patterson map using the CRYM software system. Full-matrix least-squares refinements were carried out with reflections for which $I > 2\,\sigma(I)$.

(12) Crystal data for $[M_2(dimen)_4](Y)_2$ (M = Rh, Y = TFPB; M = Rh, Y = $B(C_6H_5)_4$; M = Ir, Y = PF_6; M = Ir, Y = TFPB; M = Ir, Y = $B(C_6H_5)_4$) are included in the supporting material.

(13) From Raman studies of $M_2(TM4)_4{}^{2+}$, ground-state M−M force constants were determined to be 0.092 (M = Rh)[13a] and 0.159 mdyn Å^{-1} (M = Ir).[13b] (a) Dallinger, R. F.; Miskowski, V. M.; Gray, H. B.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 1595. (b) Smith, D. C.; Ph.D. Dissertation, California Institute of Technology, 1989.

0020-1669/96/1335-0549$12.00/0

Table 1. Solid-State Absorption and Corrected Fluorescence Maxima (nm) for $[M_2(dimen)_4](Y)_2$

M	Y	absorption[a]	emission[a]
Ir	PF_6	468	650
Ir	TFPB	534	666
Ir	$B(C_6H_5)_4$	580	710
Ir	CH_2Cl_2 soln[b]	470, 580	712
Rh	PF_6	420	550
Rh	TFPB	428	562
Rh	$B(C_6H_5)_4$	437	587
Rh	2-MeTHF:CH_3CN soln	423	600

[a] See Supporting Information for $Ir_2(dimen)_4^{2+}$ sample preparation. [b] The $M_2(dimen)_4^{2+}$ spectra are solvent and anion independent.

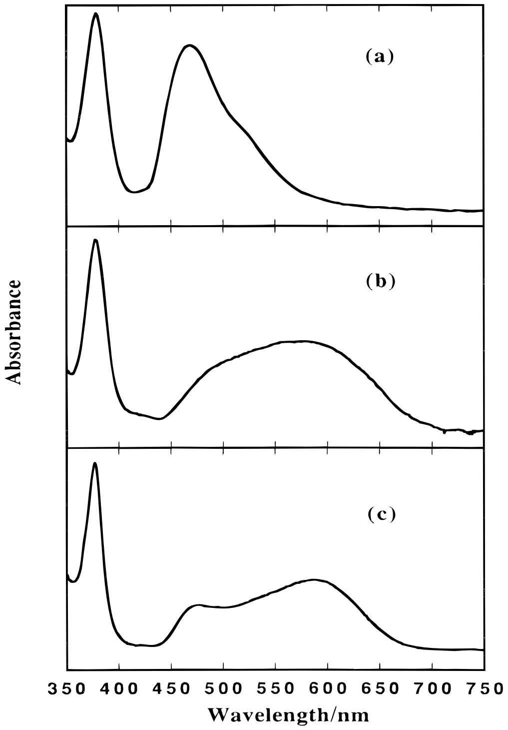

Figure 2. Solid-state UV−vis absorption spectra of $[Ir_2(dimen)_4](Y)_2$: (a) Y = PF_6; (b) Y = TFPB; (c) Y = $B(C_6H_5)_4$.

Structures of dimen complexes with M−M distances between 3.946 (Ir, $TFPB^-$) and 4.48 Å (Rh, PF_6^-) have twist angles of 0°, but the two $B(C_6H_5)_4^-$ salts have shorter $d(M_2)$ and significant twist angles, $\omega = 16.2$ (Rh) and 17.2° (Ir). These observations accord with the large (39°) twist angle found for $[Ir_2(dimen)_4(P(C_6H_5)_3)(AuP(C_6H_5)_3)](PF_6)_3$, with $d(Ir_2) = 2.986$ Å.[7c]

As the M−M distance decreases in d^8−d^8 complexes, the $^1(d\sigma^* \rightarrow p\sigma)$ absorption band red shifts.[2,13−15] This shift is more pronounced in $Ir_2(dimen)_4^{2+}$ than in the corresponding $Rh_2(dimen)_4^{2+}$ complexes (Table 1, Figure 2).[13] Fluorescence maxima for the eclipsed $[Ir_2(dimen)_4](Y)_2$ (Y = PF_6, TFPB) salts are only 370 cm^{-1} apart, but the Stokes shifts for the two compounds are very different (5940 and 3740 cm^{-1}, respectively). Interestingly, the emission data suggest that the structure of the excited singlet state of $Ir_2(dimen)_4^{2+}$ in CH_2Cl_2 solution ($\lambda_{em} \sim 712$ nm) is similar to that of crystalline $[Ir_2(dimen)_4][B(C_6H_5)_4]_2$ ($\lambda_{em} \sim 710$ nm; ground-state twist angle = 17°).

The ground-state potential energy surface that controls the net M−M interaction is determined by a combination of *four* major distortion coordinates:[16] (**1**) pure metal−metal stretching, with a minimum at 3.1−3.3 Å (based on the $M_2(TM4)_4^{2+}$ structures);[13b,14] (**2**) ligand flexing (minimum at $d(M-M) \approx 5.2$ Å); (**3**) out-of-plane bending (θ) (primarily composed of δ(*trans*-C−M−C) and δ(N−C−M) modes of local a_{2u} symmetry with an energy minimum at 0° relative to square-planar geometry); (**4**) a twisting motion (ω) that rotates one square plane with respect to the other from a minimum at 0° (eclipsed NC groups).[17] We suggest that an important intersection of these distortion coordinates occurs at $d(M-M) \approx 3.9$ Å, between the M−M distances of the eclipsed $[Ir_2(dimen)_4](TFPB)_2$ and twisted $[Rh_2(dimen)_4[B(C_6H_5)_4]_2$ structures. M−M distances greater than 3.9 Å are accommodated by trade-offs between ligand flexing and "a_{2u}" out-of-plane bending that maintains the eclipsed conformation. M−M distances shorter than 3.9 Å are produced by relaxing the out-of-plane bending of the square planes through the torsional deformation (ω) to a twisted conformation.

We considered the possibility that the solid-state structures of the cations are "snapshots" along a flat multidimensional energy surface with no well defined minima; if this were the case, our structures would be another example of the Bürgi−Dunitz structure correlation principle.[18] Although $Rh_2(dimen)_4^{2+}$ can be described in this way,[16] its iridium analogue cannot: solutions of $Ir_2(dimen)_4^{2+}$ show *two* absorption maxima (480 (ϵ 6000) and 575 nm (ϵ 7300 M^{-1} cm^{-1})) attributable to $^1(d\sigma^* \rightarrow p\sigma)$ excitation. The relative intensities of these bands depend on temperature, with the band at higher energy losing intensity to the band at lower energy as the temperature is decreased.[19] Moreover, resonance Raman spectra[20] show bands due to two different ν(Ir−Ir) stretches, whose intensities depend on the excitation wavelength: the lower-frequency stretch is enhanced with excitation into the higher-energy $^1(d\sigma^* \rightarrow p\sigma)$ band, while the higher-frequency stretch is enhanced with excitation into the lower-energy $^1(d\sigma^* \rightarrow p\sigma)$ system. Thus the spectroscopic and structural evidence, taken together, confirms that the ground-state potential energy surface of $Ir_2(dimen)_4^{2+}$ possesses at least two relatively deep minima. It also would appear that the solution structures of the Ir_2 (short) and Ir_2 (long) deformational isomers are very similar to those found in the crystalline $B(C_6H_5)_4^-$ and PF_6^- salts.

Acknowledgment. Work at the University of Minnesota and the California Institute of Technology was supported by the National Science Foundation. We thank Johnson Matthey for generous loans of rhodium trichloride and iridium trichloride.

Supporting Information Available: Text giving crystal data, experimental procedures for solid state spectroscopic measurements, and a discussion of the treatment of ligand disorder, atomic numbering diagrams and ORTEP drawings of the cations in $[Rh_2(dimen)_4](TFPB)_2$ and $[Ir_2(dimen)_4](TFPB)_2$, tables of X-ray crystallographic data, positional parameters, bond distances and angles, and thermal parameters for $[Rh_2(dimen)_4](Y)_2$ (Y = TFPB, $B(C_6H_5)_4$) and $[Ir_2(dimen)_4](Y)_2$ (Y = PF_6, TFPB, $B(C_6H_5)_4$), and ORTEP diagrams of $Ir_2(dimen)_4^{2+}$ cations from $[Ir_2(dimen)_4](PF_6)_2$ and $[Ir_2(dimen)_4][B(C_6H_5)_4]_2$ (193 pages). Ordering information is given on any current masthead page.

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(19) We have analyzed the temperature dependence of these spectra: assuming $Ir_2 \text{(long)} \rightleftharpoons Ir_2 \text{(short)}$, we calculate $\Delta H° = -0.8$ kcal/mol and $\Delta S° = 1.44$ cal/(mol K).

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