Supporting Information

for

Mononuclear Cu/O₂ Complexes: Geometries, Spectroscopic Properties, Electronic Structures, and Reactivity

Christopher J. Cramer* and William B. Tolman*

Department of Chemistry, Supercomputer Institute, and Center for Metals in Biocatalysis, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55410

* Corresponding authors: cramer@chem.umn.edu, tolman@chem.umn.edu

Table S1. Selected O-O distances, stretching frequencies (ν), and $1/\nu^{2/3}$ values for O_2^n species (data plotted in Figure 3).

Complex	O-O (exp, Å)	O-O (calc, Å)	$\nu(\text{O-O})$ (exp, cm^{-1})	$\nu(\text{O-O})$ (calc, cm^{-1})	$1/\nu^{2/3}$ (exp, $\text{cm}^{2/3}$)	$1/\nu^{2/3}$ (calc, $\text{cm}^{2/3}$)	Ref
O_2^+	1.123	1.122	1858	1946	0.0066166	0.0064156	i,ii
O_2 (triplet)	1.208	1.220	1549	1550	0.0074696	0.0074664	iii,iv
O_2 (singlet)	1.216		1484		0.0076862		v,vi
TpCuO_2^a (1a)	1.220	1.329	1112	1124	0.0093167	0.0092503	iv,vii
(TMGtren) CuO_2^b (2)	1.280	1.322	1117	1111	0.0092889	0.0088653	viii
$(\text{Tp}')_2\text{SmO}_2^c$	1.319		1124		0.0092503		ix
$\text{Tp}''\text{Cr}(\text{Cl})\text{O}_2^d$	1.325	1.339	1104	1086	0.0093617	0.0094648	iv,x
$\text{Tp}''\text{Cr}(\text{pzH})\text{O}_2^d$	1.327		1072		0.0095471		x
NaO_2	1.330	1.369	1094	1087	0.0094186	0.0094590	iv,xi
TpCoO_2^e	1.355	1.380	961	987	0.0102690	0.0100880	iv,xii
$\text{Tp}''\text{Cr}(\text{Ph})\text{O}_2^d$		1.361	1027	1034	0.0098240	0.0097796	iv,x
O_2^-		1.363	1090	1097	0.0094417	0.0094015	iv,xiii
LiO_2		1.364	1097	1097	0.0094015	0.0094015	iii,iv
$(\text{R}_4\text{por})\text{MnO}_2^f$		1.377	983	1009	0.0101150	0.0099404	iv,xiv,xv
NiO_2		1.382	966	982	0.0102330	0.0101220	iv,xvi
$\text{tBu}_2\text{L}^{\text{iPr}_2}\text{CuO}_2$ (3b)	1.390	1.376	961	1013	0.0102690	0.0099143	iv,xvii,xviii
(anilidoimine) CuO_2 (4)	1.392	1.358	974	1041	0.0101770	0.0097357	xix
$(\text{bc})\text{PdO}_2^g$	1.411	1.400	891	941	0.0108000	0.0104140	xx
$[(\text{R}_4\text{por})\text{MnO}_2]^{-f}$	1.421	1.430		937		0.0104430	iv,xiv,xv
$[(\text{TIMEN}^{\text{xy1}})\text{CoO}_2]\text{BPh}_4^h$	1.429		890		0.0108080		xxi
$\text{Tp}''\text{Mn}(\text{pzH})\text{O}_2^d$	1.430		892		0.0107920		xxii
H_2O_2	1.453	1.471	880	892	0.0108900	0.010792	xxiii,xxiv
$[(\text{tmen})_2\text{CoO}_2]\text{ClO}_4^i$	1.457		861		0.0110490		xxv
BrAlO_2		1.691	524	543		0.0150250	iv,xxvi

^a Tp = tris(3-isopropyl-5R-pyrazolyl)hydroborate, where R = tBu (exp) or H (calc). ^b TMG = tris(tetramethylguanadino)tren. ^c Tp' = tris(3,5-dimethylpyrazolyl)hydroborate. ^d Tp'' = tris(3-methyl-5-tert-butylpyrazolyl)hydroborate. ^e Tp defined as in *a*, with R = tBu. ^f R₄por = tetra-R-porphyrin, where R = Ph (exp) or H (calc). ^g bc = bathocuproine. ^h TIMEN^{xy1} = (tris[2-(3-alkylimidazol-2-ylidene)ethyl]amine with xylyl substituents. ⁱ tmen = tetramethylethylenediamine.

References

- ⁱ v(O-O): Shamir, J.; Binenboym, J.; Claassen, H. H., *J. Am. Chem. Soc.* **1968**, *90*, 6223-6224.
- ⁱⁱ O-O distance: Abrahams, S. C., *Q. Rev. Chem. Soc.* **1956**, *10*, 407-436.
- ⁱⁱⁱ Andrews, L.; Smadzewski, R. R., *J. Chem. Phys.* **1973**, *68*, 2258-2261.
- ^{iv} Cramer, C. J.; Tolman, W. B.; Theopold, K. H.; Rheingold, A. L., *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 3635-3640.
- ^v Kasha, M.; Khan, A. U., *Ann. N. Y. Acad. Sci.* **1970**, *171*, 5-23.
- ^{vi} Herzberg, L.; Herzberg, G., *Astrophys. J.* **1947**, *105*, 353-359.
- ^{vii} Fujisawa, K.; Tanaka, M.; Moro-oka, Y.; Kitajima, N., *J. Am. Chem. Soc.* **1994**, *116*, 12079-12080.
- ^{viii} (a) Schatz, M.; Raab, V.; Foxon, S. P.; Brehm, G.; Schneider, S.; Markus Reiher; Holthausen, M. C.; Sundermeyer, J.; Schindler, S., *Angew. Chem. Int. Ed.* **2004**, *43*, 4360-4363. (b) Würtele, C.; Gaoutchenova, E.; Harms, K.; Holthausen, M. C.; Sundermeyer, J.; Schindler, S., *Angew. Chem. Int. Ed.* **2006**, *45*, 3867-3869.
- ^{ix} Zhang, X.; Loppnow, G. R.; McDonald, R.; Takats, J., *J. Am. Chem. Soc.* **1995**, *117*, 7828-7829.
- ^x (a) Qin, K.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H., *Angew. Chem. Int. Ed.* **2002**, *41*, 2333-2335. (b) Qin, K.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H., unpublished results.
- ^{xi} Smardzewski, R. R.; Andrews, L., *J. Chem. Phys.* **1972**, *57*, 1327-1333.
- ^{xii} Egan, J., J. W.; Haggerty, B. S.; Rheingold, A. L.; Sendlinger, S. C.; Theopold, K. H., *J. Am. Chem. Soc.* **1990**, *112*, 2445-2446.
- ^{xiii} Rolfe, J.; Holzer, W.; Murphy, W. F.; Bernestein, J. H., *J. Chem. Phys.* **1968**, *49*, 963-975.
- ^{xiv} Urban, M. W.; Nakamoto, K.; Basolo, F., *Inorg. Chem.* **1982**, *21*, 3406-3408.
- ^{xv} VanAtta, R. B.; Strouse, C. E.; Hanson, L. K.; Valentine, J. S., *J. Am. Chem. Soc.* **1987**, *109*, 1425-1434.
- ^{xvi} Huber, H.; Ozin, G. A., *Can. J. Chem.* **1972**, *50*, 3746-3747.
- ^{xvii} Spencer, D. J. E.; Aboelella, N. W.; Reynolds, A. M.; Holland, P. L.; Tolman, W. B., *J. Am. Chem. Soc.* **2002**, *124*, 2108-2809.
- ^{xviii} Aboelella, N. W.; Lewis, E. A.; Reynolds, A. M.; Brennessel, W. W.; Cramer, C. J.; W. B. Tolman, *J. Am. Chem. Soc.* **2002**, *124*, 10660-10661.
- ^{xix} Reynolds, A. M.; Gherman, B. F.; Cramer, C. J.; Tolman, W. B., *Inorg. Chem.* **2005**, *44*, 6989-6997.
- ^{xx} Stahl, S. S.; Thorman, J. L.; Nelson, R. C.; Kozee, M. A., *J. Am. Chem. Soc.* **2001**, *123*, 7188-7189.
- ^{xxi} Hu, X.; Castro-Rodriguez, I.; Meyer, K., *J. Am. Chem. Soc.* **2004**, *126*, 13464-13473.
- ^{xxii} Kitajima, N.; Komatsuzaki, H.; Hikichi, S.; Osawa, M.; Moro-oka, Y., *J. Am. Chem. Soc.* **1994**, *116*, 11596-11597.
- ^{xxiii} Blunt, F. J.; Hendra, P. J.; Mackenzie, J. R., *J. Chem. Soc. Chem. Commun.* **1969**, 278.
- ^{xxiv} Busing, W. R.; Levy, H. A., *J. Chem. Phys.* **1965**, *42*, 3054-3059.
- ^{xxv} Rahman, A. F. M. M.; Jackson, W. G.; Willis, A. C., *Inorg. Chem.* **2004**, *43*, 7558-7560.
- ^{xxvi} Bahlo, J.; Himmel, H.-J.; Schnöckel, H., *Inorg. Chem.* **2002**, *41*, 4488-4495.