

self-exchange rate constant calculated by Margerum and co-workers from the  $\text{Cu}(\text{dmp})_2^{2+}-\text{IrCl}_6^{2-}$  reaction ( $9.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>3</sup> is considerably larger, however, even after making electrostatic corrections ( $1.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ). Surprisingly good agreement exists between our  $k_{11}^{\text{cor}}(\text{Cu}(\text{dpmp})_2^{2+/3-})$  value and the self-exchange rate constant derived from the  $\text{Cu}(\text{dpmp})_2^{3-}-\text{IrCl}_6^{2-}$  reaction ( $3.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ;<sup>3</sup>  $1.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  obtained by correcting for noncancelling electrostatic work terms). Chloride bridging, reported recently in the oxidation of copper(II)-peptide complexes by  $\text{IrCl}_6^{2-}$ ,<sup>13</sup> or other non-electrostatic stabilization of the precursor complex in the  $\text{Cu}(\text{dmp})_2^{2+}-\text{IrCl}_6^{2-}$  reaction may be partially responsible for the discrepancy between our  $k_{11}(\text{Cu}(\text{dmp})_2^{2+/+})$  value and that reported by Margerum et al.<sup>3</sup>

Quantitative understanding of the redox reactivity difference between the  $\text{Cu}(\text{dmp})_2^{2+/+}$  and  $\text{Cu}(\text{dpmp})_2^{2-/3-}$  couples is made difficult by the approximate nature of the Marcus calculations, the nonspherical structures of the reactants, and the likelihood that changes in both the coordination geometry and number of copper accompany the conversion of Cu(II) to Cu(I). The 4,7-benzenesulfonate substituents should reduce the outer-sphere rearrangement contribution to  $\Delta G_{11}^{\text{cor}}$  in  $\text{Cu}(\text{dpmp})_2^{2-/3-}$  relative to  $\text{Cu}(\text{dmp})_2^{2+/+}$ . With the assumption that the  $\text{C}_6\text{H}_5\text{SO}_3^-$  substituents contribute 4.5 Å to the radius ( $r$ ) of  $\text{Cu}(\text{dpmp})_2^{3-/2-}$  (11.5 Å),<sup>12</sup> approximate outer-sphere rearrangement activation free energies of 2.0 kcal/mol for this couple and 3.2 kcal/mol for  $\text{Cu}(\text{dmp})_2^{2+/+}$  are obtained from eq 4,<sup>14</sup> where  $n$  is the number of electrons transferred (1). It

$$\Delta G^*_0 = 22.7n^2/r \quad (4)$$

should be noted that this expression pertains rigorously only to self-exchange reactions of spherically symmetric ions in water at 25 °C. We estimate, therefore, that the outer-sphere rearrangement requirement accounts for ca. 1.2 kcal/mol of the 2.6 kcal/mol difference between  $\Delta G_{11}^{\text{cor}}$  values for the two Cu(I,II) couples.

Other factors which should be considered in comparing the redox reactivities of the  $\text{Cu}(\text{dpmp})_2^{2-/3-}$  and  $\text{Cu}(\text{dmp})_2^{2+/+}$  couples include changes in coordination geometry, ligand field stabilization energy, and coordination number required to bring the reactants into the activated complex. The coordination geometries of  $\text{Cu}(\text{dmp})_2^{2+}$  and  $\text{Cu}(\text{dmp})_2^+$  are flattened tetrahedral and tetrahedral, respectively,<sup>15</sup> and strong evidence has been presented that the former ion is five-coordinate ( $[\text{Cu}(\text{dmp})_2(\text{H}_2\text{O})]^{2+}$ ) in aqueous solution.<sup>8,16</sup> The closeness of  $\text{Cu}(\text{dmp})_2^{2+}$  and  $\text{Cu}(\text{dpmp})_2^{2-}$   $E^\circ$  values<sup>3</sup> indicates that *net* changes in coordination number and geometry associated with reduction of these complexes must be comparable. Analogous changes associated with the activation process need not be identical, however, particularly with respect to the extent of  $\text{Cu}^{\text{II}}-\text{H}_2\text{O}$  bond breaking in the activated complex. Al-Shatti et al.<sup>8</sup> propose that the reduction of  $\text{Cu}(\text{dpmp})_2^{2+}$  by  $\text{Fe}(\text{CN})_6^{4-}$  occurs via an activated intermediate, generated through the displacement of water from  $[\text{Cu}(\text{dpmp})_2(\text{H}_2\text{O})]^{2+}$  to form a reactive tetrahedral species. While our kinetic data do not require complete displacement of  $\text{H}_2\text{O}$  from the first coordination sphere of Cu(II) in the activated complexes for reduction of  $\text{Cu}(\text{dpmp})_2^{2-}$  and  $\text{Cu}(\text{dmp})_2^{2+}$  by  $\text{HQ}^-$ ,  $\text{Cu}^{\text{II}}-\text{H}_2\text{O}$  bond breaking is, no doubt, an important (and variable) aspect of the electron-transfer mechanism. Indeed, differences between the extent of  $\text{Cu}^{\text{II}}-\text{H}_2\text{O}$  bond breaking (and  $\text{Cu}^{\text{I}}-\text{H}_2\text{O}$  bond making) in the activated complexes of self-exchange and cross reactions probably are largely responsible for the notable

lack of consistency among  $k_{11}$  values calculated for copper-(I,II)-phenanthroline couples from the Marcus relationship. Thus, a  $k_{11}$  value derived from the reduction rate of a copper(II)-phenanthroline complex will be lower than the actual value if the extent of  $\text{Cu}^{\text{II}}-\text{H}_2\text{O}$  bond breaking in the rate-limiting step exceeds that required in the self-exchange reaction. Consistent  $k_{11}$  values from reduction and oxidation cross reactions may in fact be obtained for Cu(I,II) couples under conditions where solvation of Cu is precluded, i.e., in the blue copper protein stercyanin.<sup>17</sup>

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**Registry No.**  $\text{Cu}(\text{dpmp})_2^{2-}$ , 72244-80-5;  $\text{Cu}(\text{dmp})_2^{2+}$ , 14875-91-3;  $\text{H}_2\text{Q}$ , 123-31-9.

(17) Holwerda, R. A.; Knaff, D. B.; Gray, H. B.; Clemmer, J. D.; Crowley, R.; Smith, J. M.; Mauk, A. G. *J. Am. Chem. Soc.* **1980**, *102*, 1142.

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### Dioxygen Complexes of Ruthenium(III) in Aqueous Solution

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The dioxygen complexes of transition-metal ions have been extensively studied during the last decade.<sup>1-4</sup> The most important areas of research in metal dioxygen chemistry have been the cobalt(II) dioxygen complexes,<sup>3</sup> the picket fence and picket fence type of iron(II) porphyrin oxygen complexes,<sup>2</sup> and the manganese(II) porphyrin complexes.<sup>4</sup> The platinum group metal ions, rhodium(I), iridium(I), ruthenium(0), platinum(0), and palladium(0), are sufficiently soft and give<sup>1,5,6</sup> metal dioxygen complexes mostly with soft donors such as tertiary phosphines, arsines, etc. The only example of a hard donor such as EDTA as a ligand in metal-dioxygen complexes is the complex<sup>7</sup>  $\text{Ti}(\text{EDTA})\text{O}_2^{2-}$ . To our knowledge, except for the cobalt(II) dioxygen complexes,<sup>3</sup> equilibrium and other studies have not been conducted on any other metal dioxygen system in aqueous solution. Besides, there are no examples of a platinum group metal-dioxygen complex with hard donor ligands such as EDTA and HEDTA. In the present investigation ruthenium(III) dioxygen complexes are reported for the hard donor ligands EDTA and HEDTA in aqueous solution.

The potentiometric titrations of 1:1  $\text{Ru}^{\text{III}}-\text{EDTA}$  and  $\text{Ru}^{\text{III}}-\text{HEDTA}$  systems were conducted with continuous bubbling of oxygen through the experimental solutions. The  $\text{Ru}^{\text{III}}-\text{EDTA}$  and  $\text{Ru}^{\text{III}}-\text{HEDTA}$  systems gave inflections at  $a = 2.5$  and 4.5, respectively, indicative<sup>3</sup> of the formation of binuclear  $\mu$ -hydroxo- $\mu$ -peroxo complexes in solution. The pH of the solution was measured in each case after sufficient time

(13) Owens, G. D.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 1446.

(14) Reynolds, W. L.; Lumry, R. W. "Mechanisms of Electron Transfer"; Ronald Press: New York, 1966; p 129.

(15) Hall, J. R.; Marchant, N. K.; Plowman, R. A. *Aust. J. Chem.* **1963**, *16*, 34.

(16) Davies, G.; Higgins, R.; Loose, D. J. *Inorg. Chem.* **1976**, *15*, 700.

(1) Taqui Khan, M. M.; Martell, A. E. "Homogeneous Catalysis by Metal Complexes"; Academic Press: New York, 1974; Vol. 1.

(2) "Metal Ion Activation of Dioxygen"; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1980.

(3) McLendon, G.; Martell, A. E. *Coord. Chem. Rev.* **1976**, *19*, 1 and references therein.

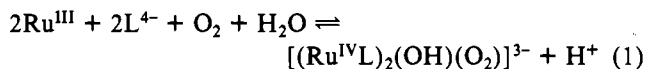
(4) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139.

(5) Vaska, L. *Acc. Chem. Res.* **1976**, *1*, 175.

(6) Choy, V. J.; O'Connor, C. J. *Coord. Chem. Rev.* **1972**, *9*, 145.

(7) Kristine, F. J.; Shepherd, R. E. *J. Chem. Soc., Chem. Commun.* **1980**, 132.

was allowed for equilibration.<sup>8</sup> The stability constants  $\log K_{ML}^{M,L,H_2O,O_2} (ML)_2(OH)(O_2^{2-})$  at 35 °C and  $\mu = 0.1$  (KCl) corresponding to equilibrium 1, calculated for L = EDTA and HEDTA, are  $29.84 \pm 0.15$  and  $22.13 \pm 0.16$ , respectively.



The titration of Ru<sup>III</sup>-EDTA and Ru<sup>III</sup>-HEDTA systems were also conducted under nitrogen atmosphere after sufficient time was given for equilibration.<sup>8</sup> Under these conditions, the systems Ru<sup>III</sup>-EDTA and Ru<sup>III</sup>-HEDTA show a simultaneous liberation of 2 and 4 protons, respectively, followed by the hydrolysis of the complexes in the higher buffer region. The stability constants  $\log K_{ML}$  at 35 °C and  $\mu = 0.1$  M (KCl) calculated for Ru<sup>III</sup>-EDTA and Ru<sup>III</sup>-HEDTA systems are  $13.8 \pm 0.1$  and  $10.4 \pm 0.1$ , respectively. The species ML in solution are expected to be mixed-ligand complexes of Ru(III) with EDTA and HEDTA of the composition  $[Ru(L)Cl]^{2-}$  (L = EDTA, HEDTA) with at least one coordinated chloride ion in the coordination sphere of the metal ion. The existence of such complexes in solution was already reported earlier.<sup>9,10</sup> The lower stabilities of these mixed-ligand complexes compared to those of Fe<sup>III</sup>-EDTA<sup>11</sup> and -HEDTA<sup>12,13</sup> systems are expected on the basis of a larger ionic size of Ru(III) as compared to Fe(III) and due to the presence of the coordinated chloride ion in the coordination sphere of metal ion. In these systems, the ligands EDTA and HEDTA possibly act as pentadentate<sup>12</sup> ligands with a vacant coordination site on the metal ion occupied by a chloride ion. At higher pH, hydrolysis of the complexes takes place due to the replacement of the coordinated Cl<sup>-</sup> by H<sub>2</sub>O, which loses a proton to form a hydroxo species according to equilibrium 2.



The pK(OH) values for the formation of  $[Ru(L)(OH)]^{2-}$  species were calculated to be  $5.67 \pm 0.02$  and  $5.38 \pm 0.02$  for L = EDTA and HEDTA, respectively.

In the presence of oxygen, ruthenium(III) formally gets oxidized to ruthenium(IV) and facile displacement of the chloride ion takes place from the coordination sphere of the metal ion to form the  $\mu$ -hydroxo- $\mu$ -peroxo species. The number of oxygen molecules bound per mole of the metal chelate was determined from the oxygen-uptake measurements conducted with a Validyne Corp. differential pressure transducer calibrated with a cobalt(II)-diene-oxygen system as a reference.<sup>3</sup> For both Ru<sup>III</sup>-EDTA and Ru<sup>III</sup>-HEDTA systems, 1 mol of oxygen is absorbed per 2 mol of the metal ion, supporting the formation of a bridged peroxo species in solution. On acidification of the oxygenated complexes, 1 mol of H<sub>2</sub>O<sub>2</sub> is released per mol of the complex, indicative of the presence of peroxo species in the complexes. The released H<sub>2</sub>O<sub>2</sub> was estimated by an iodometric procedure.<sup>14</sup>

In the presence of excess oxygen, the pseudo-first-order rate constants  $k_1$   $[[O_2] \gg [Ru^{III}]]$  at 35 °C ( $\mu = 0.1$  M (KCl)) with respect to the metal ligand dioxygen complex formation for Ru<sup>III</sup>-EDTA-O<sub>2</sub> and Ru<sup>III</sup>-HEDTA-O<sub>2</sub> complexes are  $k_1 = 1.5 \times 10^{-3} \text{ s}^{-1}$  ( $t_{1/2} = 7.7$  min) and  $k_1 = 1.2 \times 10^{-3} \text{ s}^{-1}$  ( $t_{1/2} = 9.7$  min), respectively. The rates were determined by oxygen-uptake measurements using 10 mL of complex solution of various concentrations below  $10^{-3}$  M (at pH  $\sim 4.5$ ) in a

Table I. Electronic Absorption Spectra of Ru(III) Complexes in 0.1 M KCl

system	$\lambda_{max}$ , nm ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )	
	under N <sub>2</sub> atm	after oxygenation
Ru <sup>III</sup> -EDTA	283 (2920), 312-316 (1718)	295 (2480), 317 (1862), 331 (663), 345 (728), 394 (2760)
Ru <sup>III</sup> -HEDTA	296 (2120), 312 (1763)	280-288 (2480), 310 (1658), 320 (1612), 345 (709), 431 (640)

closed cell of 250-mL capacity filled with oxygen at atmospheric pressure.

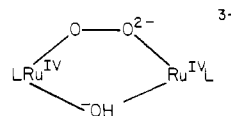
The oxygen-uptake measurements were carried out at pH 4.5 since the formation of the dioxygen complex is complete at that pH (inflection point in the pH titration curves). At higher pH values, the rate is lowered due to the formation of hydroxo species which are less reactive toward combination with dioxygen.

The oxygenated Ru<sup>III</sup>-EDTA complex gives a well-defined anodic-cathodic reversible wave at a dropping-mercury electrode vs. a saturated calomel electrode. The  $E_{1/2}$  potential was calculated to be  $-0.098$  V, the logarithmic analysis of which gave a slope of 0.033 V. The redox wave of the oxygenated species indicates the reduction of a formal Ru(IV) ion in the  $\mu$ -peroxo complex to the Ru(III) state.

The electronic absorption spectra of Ru<sup>III</sup>-EDTA and Ru<sup>III</sup>-HEDTA complexes in the presence and absence of oxygen are given in Table I. The absorption bands at 283 ( $\epsilon$  2920), and 312-316 nm ( $\epsilon$  1718 M<sup>-1</sup> cm<sup>-1</sup>) in Ru<sup>III</sup>-EDTA and 296 ( $\epsilon$  2120) and 312 nm ( $\epsilon$  1763) in Ru<sup>III</sup>-HEDTA systems are ligand charge-transfer bands. A similar band is observed<sup>9</sup> in the Ru<sup>II</sup>-Hedta-H<sub>2</sub>O complex at 282 nm ( $\epsilon$  3120).

The oxygenated complexes retain the ligational bands of EDTA and HEDTA observed in the Ru(III) complexes with slight shifts. In the oxygenated complexes, the bands at 331 ( $\epsilon$  663) and 345 nm ( $\epsilon$  728) in the EDTA and 320 ( $\epsilon$  1612) and 345 nm ( $\epsilon$  709) in HEDTA complexes may be assigned to the  $1\pi^*(O_2) \rightarrow d\sigma^*$  LMCT transition.<sup>15</sup> The bands at 394 ( $\epsilon$  2760) and 431 nm ( $\epsilon$  640) in the EDTA and HEDTA complexes are d-d transitions in Ru(IV) with considerable charge-transfer character. A similar band is observed at 472 nm<sup>16</sup> ( $\epsilon \sim 700$ ) in the aquo-ruthenium(IV) system in HClO<sub>4</sub> medium. These bands are characteristic of Ru(IV) and are not observed for the Ru(III) species which give very low intensity d-d bands around 600 nm.

On the basis of potentiometric, oxygen-uptake, polarographic, and spectral studies, the ruthenium(III)-dioxygen complexes can be formulated as



(where L = EDTA, HEDTA) with a formal oxidation state of +4 for the metal ion. If EDTA and HEDTA occupy five coordination positions on the metal ion, then the Ru(IV) ion will have a coordination number of 7. This is expected because the oxidative addition of Ru<sup>II</sup> (d<sup>6</sup>) to the Ru<sup>IV</sup> (d<sup>4</sup>) configuration usually results in coordination number 7 for Ru(IV). Thus Ru(CP)<sub>2</sub> adds I<sub>2</sub> to form the seven-coordinate<sup>14</sup> Ru(IV) species Ru(CP)<sub>2</sub>I<sup>+</sup>.

The dioxygen complexes were isolated in the form of their tetraethylammonium salts:  $[(RuL)_2(OH)(O_2)](Et_4N)_3$ . The

(8) Stanbury, D. M.; Haas, O.; Taube, H. *Inorg. Chem.* **1980**, *19*, 518.

(9) Diamantis, A. A.; Dubrawski, J. V. *Inorg. Chem.* **1981**, *20*, 1142.

(10) Scherzer, Jellus; Clapp; Leallyn, B. J. *Inorg. Nucl. Chem.* **1968**, *30* (4), 1107-1109.

(11) Kolltoff, I. M.; Clemens, Averbach. *J. Am. Chem. Soc.* **1952**, *74*, 1452 and references therein.

(12) Skochdopole, R.; Chaberek, S. *J. Inorg. Nucl. Chem.* **1959**, *11*, 222-233.

(13) Schwarzenbach, G. *Helv. Chim. Acta* **1949**, *32*, 839.

(14) Haim, A.; Wilmarth, W. K. *J. Am. Chem. Soc.* **1961**, *83*, 509.

(15) Lever, A. B. P.; Gray, H. B. *Acc. Chem. Res.* **1978**, *11*, 348.

(16) Wehner, P.; Hindman, J. C. *J. Am. Chem. Soc.* **1950**, *72*, 3911.

$\nu(\text{O}_2)$  of these complexes is observed around  $890\text{ cm}^{-1}$ , confirming the presence of a coordinated peroxo group in the complexes. The coordinated OH gave a broad band around  $3200\text{ cm}^{-1}$ . The molar conductivities of these complexes in aqueous solution are  $392$  and  $380\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$  respectively for the EDTA and the HEDTA complexes. In the solid state the complexes are diamagnetic at room temperature. Detailed solution EPR studies of the complexes are in progress. There seems to be a spin pairing of the two unpaired spins on ruthenium(IV) by an antiferromagnetic interaction. In basic solution the complex  $[(\text{Ru}(\text{EDTA}))_2(\text{OH})(\text{O}_2)]^{3-}$  is reversible with respect to oxygen uptake on heating. The solutions on losing  $\text{O}_2$  give electronic spectra similar to those of  $\text{Ru}^{\text{III}}\text{-EDTA}$  complexes. The coordinated dioxygen in this complex cannot however be removed by purging  $\text{N}_2$  or argon through the solution.

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**Registry No.**  $[(\text{RuEDTA})_2(\text{OH})(\text{O}_2)](\text{Et}_4\text{N})_3$ , 80738-13-2;  $[(\text{RuHEDTA})_2(\text{OH})(\text{O}_2)](\text{Et}_4\text{N})_3$ , 80764-28-9.

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### Calculation of the $^{13}\text{C}$ NMR Paramagnetic Shielding in Tricarbonylcyclodienyliron(1+) Cations

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The generally unsatisfactory nature of the theory of  $^{13}\text{C}$  NMR shifts in organometallic systems is well documented.<sup>1,2</sup> In a previous paper,<sup>2</sup> it was shown that calculations of the  $^{13}\text{C}$  NMR paramagnetic shielding constants of the isoelectronic series tricarbonyl( $\eta$ -benzene)chromium, tricarbonyl( $\eta$ -cyclopentadienyl)manganese, tricarbonyl( $\eta$ -cyclobutadiene)iron, tricarbonyl( $\eta$ -allyl)cobalt, and tricarbonyl( $\eta$ -ethylene)nickel using the self-consistent charge and configuration molecular orbital method<sup>2</sup> and the Pople-Karplus equation<sup>3</sup> correlated the observed downfield shifts of the carbonyl ligands and the upfield shifts of the ring carbon atoms in terms of the paramagnetic shielding constant  $\sigma^p$ , without recourse to considering variations in the diamagnetic term  $\sigma^d$ . Changes in the calculated values of  $\sigma^p$  within the above series involved changes in the three terms  $\Delta E$ ,  $\langle r^{-3} \rangle_{2p}$ , and  $\sum Q_{AB}$  of the Pople-Karplus equation

$$\sigma^p = -\frac{K}{\Delta E} \langle r^{-3} \rangle_{2p} \sum Q_{AB}$$

where  $K$  is a constant,  $\Delta E$  is the average excitation energy,  $\langle r^{-3} \rangle_{2p}$  is the expectation value of the inverse cubed radius of the  $2p$  orbital, and  $Q_{AB}$  involves bond-order/density matrix terms.<sup>3</sup> Our calculations showed clearly that variations in all three terms occur, and so purely qualitative discussions based on the above equation are not likely to be very successful.

Even since publication of our paper, there have been further

	carbonyl $^{13}\text{C}$ shielding						ring $^{13}\text{C}$ shielding						$^{13}\text{C}$ shielding in free ligand					
	$\text{C}_2\text{H}_5$	$\text{C}_6\text{H}_5$	$\text{C}_7\text{H}_9$	$\text{C}_5\text{H}_5$	$\text{C}_3$	$\text{C}_6\text{H}_7$	$\text{C}_3$	$\text{C}_2/4$	$\text{C}_{1/5}$	$\text{C}_3$	$\text{C}_2/4$	$\text{C}_{1/5}$	$\text{CO}$	$\text{C}_3$	$\text{C}_2/4$	$\text{C}_{1/5}$		
$\sum Q_{AB}$	1.176	1.175	1.169	1.419	1.422	1.427	1.427	1.427	1.360	1.427	1.413	1.374	1.333	1.433	1.525	1.438		
$\langle r^{-3} \rangle_{2p}$	1.338	1.336	1.335	1.303	1.303	1.304	1.303	1.303	1.299	1.303	1.303	1.292	1.320	1.337	1.322	1.337		
$(\Delta E)^{-1}$	0.349	0.420	0.539	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.245	0.2	0.2	0.2		
$\sigma^p$	-530.1	-635.5	-812.1	-57.0	-357.8	-359.3	-359.0	-356.3	-341.1	-359.0	-356.3	-343.0	-416.2	-369.9	-389.3	-371.2		
$\delta$ (exptl)	-202.7 <sup>a</sup>	-208.12 <sup>b</sup>	-207.89 <sup>b</sup>	-90.9 <sup>a</sup>	-89.0 <sup>b</sup>	-101.35 <sup>b</sup>	-99.43 <sup>b</sup>	-102.60 <sup>b</sup>	-63.74 <sup>b</sup>	-99.43 <sup>b</sup>	-102.60 <sup>b</sup>	-92.58 <sup>b</sup>	-181.3 <sup>c</sup>	-180.7 <sup>d</sup>	-138.7 <sup>d</sup>	-180.7 <sup>d</sup>		

<sup>a</sup> Reference 13. <sup>b</sup> Reference 7. <sup>c</sup> Reference 14. <sup>d</sup> Estimated value from ref 15.

- (1) J. Evans and J. R. Norton, *Inorg. Chem.*, **13**, 3042 (1974).  
 (2) D. A. Brown, J. P. Chester, N. J. Fitzpatrick and I. J. King, *Inorg. Chem.*, **16**, 2497 (1977).  
 (3) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).