band widths were similar to those found for normal human HbA.[6] In samples of $^{12}C^{16}O$ with ^{13}C present in natural abundance, only the 1951- and 1928-cm^{-1} bands were observed. The infrared spectrum of the carbonylated blood of Harvey I exhibited two ν_{CO} bands in a 1:1 intensity ratio at 1951 and 1928 cm^{-1} for $^{12}C^{16}O$. The infrared band at 1928 cm^{-1} thus corresponds to ^{13}CO resonance C whereas the band at 1951 cm^{-1} corresponds to resonances A and B. That all CO binding sites were saturated under the conditions of Figures 1–3 was confirmed by visible spectroscopy and by the fact that the relative intensities of the bands were not affected by longer exposure to CO, even in the presence of dithionite.

The infrared[7] and nmr parameters[2,3] for resonance C suggest an unusual chemical environment for CO in that rabbit hemoglobin component, and this is reflected in some chemical reactions we have monitored with ^{13}C nmr spectroscopy. Addition of citrate buffer (0.5 *M*, pH 4) to the rabbit hemolysate results in precipation of hemoglobin and a pronounced reduction in the intensity of resonance C relative to those of resonances A and B. The selective precipation of component C is complete at a hemolysate pH 4.8. Treatment of the hemolysate stepwise with fractional equivalents of oxidants like $K_3Fe(CN)_6$ results first in the exclusive oxidation of the heme unit corresponding to resonance C. When heme unit C has been consumed, oxidation of heme units A and B occur. Finally, partial carbonylation of rabbit oxyhemoglobin results first in the appearance of ^{13}CO resonances A and B; similarly, partial oxygenation of carbonyl hemoglobin results in the preferential displacement of ^{13}CO from heme unit C.

An analysis of the specific structural changes (*e.g.*, amino acid substitutions) and the attendant genetic aspects that cause these differences in rabbit hemoglobin properties must await examination of a larger population of rabbits. We could point out here, however, that the amino acid substitutions in these hemoglobins are electrophoretically silent in that the electrophoretic patterns of the hemoglobins from Harvey I and II are indistinguishable.[8] In addition the ^{13}C nmr spectra of carbonylhemoglobin from Harvey I and II were independent of rabbit age (6–11 months) and the frequency of bleeding.

Pulse Fourier transform ^{13}C nmr spectra were obtained at 25.2 MHz using a Varian XL-100-15 spectrometer interfaced to a Supernova computer. The Fourier transform was accomplished using 8K data points in the time domain. Samples were contained in 12-mm (o.d.) tubes and the magnetic field was stabilized using the 15.4-MHz deuterium lock signal of external D_2O. The infrared techniques were similar to those reported.[6,9] Both infrared (Perkin-Elmer Model 180 spectrometer) and visible spectra (Cary 14 spectrometer) were recorded in the same cells of 0.027-mm path length with CaF_2 windows. In infrared measurements a resolution of 3 cm^{-1} was selected to give a high signal to noise ratio while maintaining nearly true absorption intensities[10] at a scan speed of 1 cm^{-1} per 200 sec.

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N. A. Matwiyoff,* P. J. Vergamini, T. E. Needham, C. T. Gregg
Los Alamos Scientific Laboratory, University of California
Los Alamos, New Mexico 87544

J. A. Volpe, W. S. Caughey
Department of Biochemistry, Colorado State University
Fort Collins, Colorado 80521

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Structure of a Compound with a Molybdenum-to-Molybdenum Bond of Order Three and One-Half

Sir:

It is now well established that the element molybdenum in its lower valence states shows an extraordinary tendency to form multiple bonds. Bonds of order 4 are very common; they occur in the acetate, $Mo_2(O_2CCH_3)_4$,[1] and a number of other carboxylates,[2,3] in the trifluoroacetate[4] and the pyridine adduct of the trifluoroacetate,[5] in the $Mo_2Cl_8{}^{4-}$ ion,[6–8] in the $Mo_2(SO_4)_4{}^{4-}$ ion,[9,10] in $Mo_2(S_2COC_2H_5)_4$,[11] and presumably in various other compounds such as $Mo_2{}^{4+}(aq)$,[10] $[Mo_2en_4]Cl_4$,[10] $[Mo_2(CH_3CO_2C_2H_5)_4](CF_3SO_3)_4$,[12] and the $Mo_2Cl_4(PR_3)_4$ complexes.[13] There is also the quadruply bonded organometallic compound, $Mo_2(C_3H_5)_4$.[14] The existence of a triple bond in $Mo_2[CH_2Si(CH_3)_3]_6$ has been demonstrated.[15]

We wish to report the first compound containing an Mo-to-Mo bond of order 3.5. According to the molecular orbital description of a quadruple bond,[16–18] the order of the orbitals is σ, π, δ, ($\sigma_n{}^{(1)}$, $\sigma_n{}^{(2)}$, δ^*) π^*, σ^*, with eight electrons occupying the lower three orbitals, *viz.*, $\sigma^2\pi^4\delta^2$. Clearly then a species with a bond order of 3.5 should have an unpaired electron in the δ orbital and, in principle, there is an opportunity to gain detailed information about the δ bond through epr spectroscopy. Moreover, the role of the δ com-

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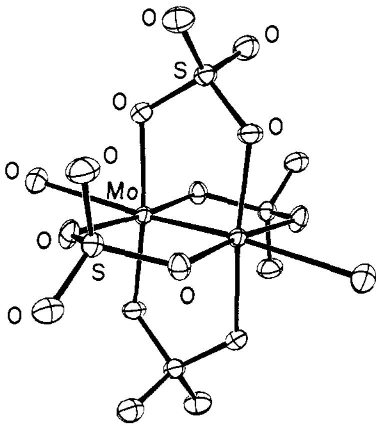

Figure 1. The structure of the $Mo_2(SO_4)_4^{3-}$ ion. Atoms are represented by their vibrational ellipsoids, contoured to enclose 50% of the electron density.

ponent of a quadruple bond in contributing to the extraordinary shortness of such bonds can be assessed by observing how the Mo–Mo bond distance changes when the bond order changes from 4.0 to 3.5 provided other factors remain essentially the same. We report here a compound in which there is an Mo–Mo bond of order 3.5 in an environment which is as nearly as possible identical with that for an Mo–Mo bond of order 4.0 in another compound.

In the course of our study of $K_4Mo_2(SO_4)_4 \cdot 2H_2O$, which forms pink rhomboidal crystals, we observed that pale red-blue crystals are also formed. The conditions under which both types of crystals can be obtained together are as follows. Bowen and Taube's compound, $K_4Mo_2(SO_4)_4$, is dissolved in 0.1 *M* H_2SO_4. This solution is allowed to mix by diffusion through a glass frit with a saturated solution of K_2SO_4 in 0.1 *M* H_2SO_4 at 25°. The system is purged of oxygen, although it cannot be said with certainty that dissolved oxygen does not play some role in the reaction. From the X-ray structure analysis the red-blue crystals were shown to have the composition $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$.

The crystals belong to the monoclinic system, space group $C2/c$, with unit cell dimensions $a = 30.654$ (4) Å, $b = 9.528$ (2) Å, $c = 12.727$ (1) Å, $\beta = 97.43$ (1)° and $Z = 8$. Using Mo $K\alpha$ radiation, 2341 reflections with $I > 3\sigma(I)$ and in the range $0 < 2\theta \leq 48°$ were collected on an automated diffractometer. The structure has been refined anisotropically to $R_1 = 0.026$ and $R_2 = 0.033$. All hydrogen atoms have been located.

There are two crystallographically independent $Mo_2(SO_4)_4^{3-}$ groups lying on crystallographic centers of symmetry. The internal dimensions of the two independent units are essentially identical. Some of the water molecules are coordinated to potassium ions, as are some of the sulfate oxygen atoms, and all hydrogen atoms form hydrogen bonds. The structure of the $Mo_2(SO_4)_4^{3-}$ unit is shown in Figure 1. Each $\overline{\text{MoOSOMo}}$ ring is folded along the O···O line, with a dihedral angle of 20 ± 3°. The disposition of these folds is such as to make the idealized symmetry C_{4h}. Each molybdenum atom is approached by the oxygen atom of a water molecule approximately along the extended Mo–Mo axis, but only at a considerable distance (2.55 Å).

Important structure parameters, averaged according to C_{4h} symmetry, are: Mo–Mo, 2.164 (3) Å; Mo–O(sulfate), 2.064 (5) Å; MoO–S, 1.521 (1) Å; S–O, 1.442 (2) Å; Mo–Mo–O, 93.6 (3)°; Mo–O–S, 121.2 (3)°; MoO–S–OMo, 105.6 (3)°; MoO–S–O, 109.0 (2)°; O–S–O, 114.7 (4)°. Tables of atomic coordinates, anisotropic thermal parameters, and complete lists of bond distances and angles are available in the microfilm edition.[19]

The $Mo_2(SO_4)_4^{3-}$ structure is qualitatively very similar to that of $Mo_2(SO_4)_4^{4-}$. All distances and angles are essentially the same except for the Mo–Mo distance, which is 0.054 (6) Å longer for the bond of lower order, and the mean Mo–OS distance, which is *ca.* 0.07 Å shorter in the present structure, as would be expected for the higher mean oxidation state of the metal atoms.

$K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$ is paramagnetic and has epr absorption with intensity corresponding to 1 ± 0.3 electron per $Mo_2(SO_4)_4^{3-}$ unit according to preliminary data. It is intended to study the spectroscopic and magnetic properties in more detail.[20]

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(19) Tables of atomic positional and anisotropic thermal parameters and a complete list of bond distances and angles will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring code number JACS-73-4431. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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F. A. Cotton,* B. A. Frenz, T. R. Webb
Department of Chemistry, Texas A&M University
College Station, Texas 77843

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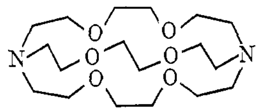
^{23}Na Nuclear Magnetic Resonance Study of Exchange Rates. Sodium Cryptate in Ethylenediamine

Sir:

We wish to report the study by ^{23}Na nmr of the exchange rate of the sodium cation between two environments in solution. In ethylenediamine (EDA) as solvent, two well-defined resonance absorptions are observed below the coalescence temperature of 50° for a sample which contains dissolved sodium bromide and half the stoichiometric amount of the hexaoxadiamine macrobicyclic complexing agent, **1**. The equilibrium constant for complex ("cryptate") formation between Na^+ and **1** in several solvents[1] is large enough that we expect little free **1** in solution. The rate of exchange in water for the case of excess **1** has been studied by proton magnetic resonance by Lehn, Sauvage, and Dietrich.[2] These authors conclude that the relatively slow rate ($k = 27$ sec^{-1} at 3°) is a measure of the rate of dissociation of the cryptate complex.



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