equilibrium quotients is provided by the drastic differences in chemical shifts of the signals due to the ethynyl hydrogen atoms of bound and free acetylene and phenylacetylene. The values obtained by this method and those obtained by the first method agreed to within 10%. Unfortunately, the resonances due to the phenyl hydrogen atoms are not appreciably shifted upon coordination and cannot be used to estimate an equilibrium quotient. A slight trend toward higher values of the equilibrium quotient seems to occur as phenyl groups are substituted for the hydrogen atoms of acetylene. While this trend could be easily rationalized, the small changes which are observed are only slightly above the estimated errors in the measurements.

The addition of gaseous HCl to solutions containing the alkyne adducts did not result in detectable amounts of alkenes. However, when $NaBH_4$ (5 mmol) was added to 5 mL of a $THF-H_2O$ (4:1) solution containing $MoO(S_2CNEt_2)_2$ (0.6 mmol) and diphenylacetylene (0.6 mmol), complete reduction of the alkyne was achieved after 3 days at ambient temperature. This reduction yielded approximately equimolar amounts of cis and trans stilbenes as shown by NMR spectroscopy. A similar reaction with acetylene was previously demonstrated[1] although some butadiene was also detected in that reaction. Furthermore, neither of the stilbenes will bind detectably to $MoO(S_2CNEt_2)_2$ in agreement with our previous results with ethylene.[1] While these complexes are capable of binding alkynes, these results make it clear that they are not capable of spontaneous reduction of the alkyne in the presence of a proton donor. In contrast, another oxomolybdenum(IV) complex, *trans*-$MoO(H_2O)(CN)_4^{2-}$, will reduce acetylene to ethylene in water.[8]

It is also noteworthy that, unlike all other complexes described herein, the product from the reaction of $MoO(S_2CNMe_2)_2$ and acetylene is particularly susceptible to reaction with adventitious O_2. We have shown that one of the products of this reaction is $Mo_2O_4(S_2CNMe_2)_2$. Others have observed[5] that the reaction of $MoO(RC_2R')(S_2CNMe_2)_2$ (R = R' = CF_3; R = H, R' = CH_3CO_2) with moist O_2 results in the formation of the dinuclear compound and *trans*-$RCH=CH(S_2CNMe_2)_2$. We presume that the reaction of our complex proceeds by the same pathway but we have not actually detected the alkene. Although commercial analyses indicated extensive, if not complete, oxidation had occurred by the time of analysis, ^1H NMR and infrared spectroscopy (Table II) have provided good evidence that the alkyne adduct is the precursor to these oxidation products.

Since oxomolybdenum(IV) is capable of binding simple alkynes, but not the corresponding alkenes, there is an obvious analogy with the action of nitrogenase with acetylene.[9] An unusual feature in our observations, however, is that a metal with a high formal oxidation state is capable of binding an alkyne to a significant degree. The explanation probably lies with an input of a significant quantity of electron density by way of π bonding from the oxo ligand as well as the sulfur donor atoms. As a result, the actual oxidation level is considerably less than would result if only σ bonding were present. It may be that similar, but not necessarily identical, π bonding in nitrogenase allows the metal to cycle between formal oxidation states which are relatively high[10] while still retaining the ability to bind relatively soft substrates to a significant degree. Similar ideas have been advanced previously.[11]

Registry No. $MoO(PhC_2Ph)(S_2CNEt_2)_2$, 68525-25-7; $MoO(PhC_2Ph)(S_2CNMe_2)_2$, 68525-26-8; $MoO(PhC_2H)(S_2CNEt_2)_2$, 68525-27-9; $MoO(HC_2H)(S_2CNMe_2)_2$, 68525-28-0; $MoO(HC_2H)(S_2CNEt_2)_2$, 66060-13-7; $MoO(S_2CNEt_2)_2$, 25395-92-0; $MoO(S_2CNMe_2)_2$, 39587-09-2.

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Synthesis, Characterization, and Magnetic Properties of Two Iron(III) Triketonates

Londa L. Borer* and William Vanderbout

The function of the iron atom in biological processes is very important; consequently various model systems have been prepared for study. Certain biologically important enzymes contain polynuclear complexes of iron. For example, complexes containing Fe–O–Fe and Fe–N–Fe linkages are common in such biological processes as oxidation–reduction reactions.[1,2] Of utmost importance are the Fe–S–Fe linkages which are the backbone of the iron–sulfur proteins. Analogues of the latter have been studied extensively in the past few years, particularly by Holm and co-workers.[3]

The ligand system chosen for this study is that of the dianionic triketone.
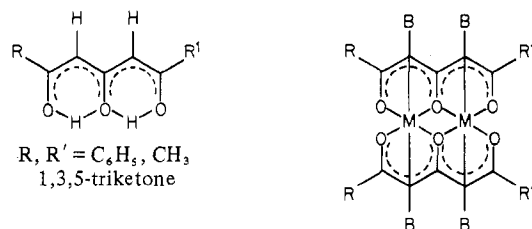
R, R' = C_6H_5, CH_3
1,3,5-triketone

M = Co(II), Cu(II), Ni(II), $V^{IV}O$
B = Py, H_2O
1,3,5-triketonates

This ligand forms binuclear complexes with metal(II) ions of the first-row transition series as shown. These binuclear metal complexes allow the study of the interaction between transition-metal ions in finite surroundings because the ions in the cluster interact strongly with each other and the interaction between molecules can be neglected. Several binuclear complexes with a variety of metal ions have been prepared and

Table I. Mössbauer Data for Iron(III) Triketonates

compound	T, K	ΔE_Q, mm/s	δ, mm/s
$Fe_2(DBA)_2(H_2O)_2(OH)_2$	297	0.71	0.37
	78	0.70	0.47
$Fe_2(BAA)_2(H_2O)_2(OH)_2$	78	0.92	0.53

studied.[4] Other complexes containing ethylenediamine (Schiff-base derivatives) have been prepared which have facilitated the study of mixed-metal binuclear species.[5] However, to our knowledge no binuclear metal(III) complex of this ligand system has been prepared and characterized; therefore it is the purpose of our work to investigate the properties of the iron(III) ion complexes with the triketones.

Experimental Section

The ligand 1,5-diphenyl-1,3,5-pentanetrione (H_2DBA) was purchased from Eastman Organic Chemical Co. Rochester, NY, and was used without further purification. 1-Phenyl-5-methyl-1,3,5-pentanetrione (H_2BAA) was prepared according to the procedures of Hauser, Miles, and Harris.[6]

$Fe_2(DBA)_2(H_2O)_2(OH)_2$. $FeCl_2 \cdot 4H_2O$ (0.75 g) was dissolved in H_2O (50 mL). Excess iron filings were added to the solution. H_2DBA (1 g) and NaOH (0.3 g) were dissolved in methanol (50 mL). The iron solution was filtered and then added to the hot ligand solution. Immediately a dark green-black precipitate appeared. The solution was stirred for approximately 15 min and cooled, and the product collected. The powdery solid was recrystallized from methanol (mp 230 °C dec). Anal. Calcd: C, 57.4; H, 4.43; Fe, 15.7. Found: C, 57.1; H, 4.6; Fe, 16.05.

$Fe_2(BAA)_2(H_2O)_2(OH)_2$. The same procedure was used as described above (mp 220 °C dec). Anal. Calcd: C, 49.4; H, 3.4; Fe, 18.7. Found: C, 49.7; H, 3.6; Fe, 19.0.

Physical Measurements. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Knoxville, TN. Iron analyses were done on a Perkin-Elmer 303 atomic absorption spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 621 spectrometer using KBr pellets. Electronic absorption spectra were recorded with 10^{-4} M methanolic solutions using a Cary 14 spectrometer. EPR spectra were recorded on a Varian E-4 spectrometer. All Mössbauer spectra were done by Professor Gary Long at the University of Missouri-Rolla, Rolla, MO. Magnetic susceptibility measurements were made by the Faraday method using $Hg[Co(SCN)_4]$ as a calibrant. Field strength of approximately 5500 G was used throughout. All calculations were made on the PDP-11 time share system at CSU-Sacramento computer center.

Results

The electronic spectra of the two chelates are similar in that they have the same general characteristics. Both have very low-intensity, broad bands in the visible region of 450–650 nm and both have a strong charge-transfer band at approximately 380 nm. The CT bands appear at 392 and 370 nm for the H_2DBA complex and the H_2BAA complex, respectively. The EPR spectrum of the solid compound gave a broad signal at $g \simeq 2.00$. This signal is comparable with that found for other polynuclear Fe(III) compounds.[7] Since some temperature dependence was observed, the EPR spectrum was also recorded in 10^{-4} M methanolic solution at various temperatures. A signal was observed at $g \simeq 4.30$ at room temperature which decreased with decreasing temperature. This signal probably is indicative of the presence of some monomeric Fe(III) impurity.[1,8]

With the assumption of high-spin iron(III) ions, the Mössbauer parameters listed in Table I are reasonable.[1,9] Further low-temperature Mössbauer studies of these two compounds should be carried out.

A spin state of $^5/_2$ is expected for these molecules since the iron ions are surrounded by six oxygen atoms in the ligand field. For two Fe(III) metal centers coupled by a superexchange mechanism, a manifold of states $S_i = 0, 1, 2, ..., 5$ is

Table II. Magnetic Data for $Fe_2(DBA)_2(H_2O)_2(OH)_2$

T, K	$10^6 \chi_g$, cgsu	$10^6 \chi_m'$,[a] cgsu	μ_{eff}, μ_B
77		22733 (exptl)	3.75 (exptl)
114	39.94	14352 (11806)[b]	3.60 (3.29)
200	27.09	9787 (10968)	3.97 (4.20)
297	21.18	7687 (9365)	4.50 (4.73)
323	21.09	7489 (8958)	4.83 (4.83)
343	18.81	6848 (8660)	4.96 (4.89)

[a] Includes a diamagnetic correction of -1.66×10^{-4} cgsu.
[b] Includes no monomeric Fe(III) impurity corrections. Least-squares fit of $J = -17.82$ cm^{-1}.

Table III. Magnetic Data for $Fe_2(BAA)_2(H_2O)_2(OH)_2$

T, K	$10^6 \chi_g$, cgsu	$10^6 \chi_m'$,[a] cgsu	μ_{eff}, μ_B
114	36.94	11026 (7686)[b]	3.18 (2.66)
200	25.42	7606 (7815)	3.50 (3.55)
273	19.82	5847 (7475)	3.58 (4.06)
297	19.02	5724 (7320)	3.70 (4.19)
343	16.68	5062 (6990)	3.74 (4.37)

[a] Includes a diamagnetic correction of -1.37×10^{-4} cgsu.
[b] Includes no monomeric Fe(III) impurity correction. Least-squares fit of $J = -20.6$ cm^{-1}.

generated. The exchange expression for such a d^5-d^5 high-spin system is as follows ($x = -J/kT$ and Θ = Weiss constant):

$$X_M = [g^2\beta^2 N[\exp(2x) + 5\exp(6x) + 14\exp(12x) + 30\exp(20x) + 55\exp(30x)]/k(T - \Theta)[1 + 3\exp(2x) + 5\exp(6x) + 7\exp(12x) + 9\exp(20x) + 11\exp(30x)]] + N\alpha$$

Using the magnetic susceptibility data of the complexes given in Tables II and III and assuming $N\alpha = 0$, $g = 2.00$, and $\Theta = 0$, we used a least-squares-fitting computer program to calculate a J value of -17.82 cm^{-1} for the DBA complex and a J value of -20.6 cm^{-1} for the BAA complex. Acceptable agreement between the observed and calculated behavior of the magnetic susceptibility and the magnetic moment cannot be obtained by increasing or decreasing J. This magnetic behavior can be accounted for by assuming some monomeric, high-spin Fe(III) complex in combination with the spin–spin coupled dimer.[7]

Discussion

To make some reasonable structural predictions about the iron(III) triketonates, we looked at several structural studies which have been completed on binuclear Cu(II), Ni(II), and Co(II) complexes of the triketones.[5] The metal–chelate framework of each is found to be approximately planar. The coordination number of the Cu(II) complexes is 5 while that of Ni(II) and Co(II) complexes is 6. The fifth and sixth coordination sites are occupied by solvent molecules. The M–M distances within the molecules range from 3.06 Å for Cu(II) to 3.272 Å for Co(II). This is considered too long for any direct metal to metal interaction. The M–O–M angle is also important if we are to consider interactions. That angle only varies from 101.5 to 103.7° for those compounds that were studied. Therefore, it can be concluded that the angle is probably invariant for other complexes of this ligand also.

On the basis of the above structural data of the Cu(II), Ni(II), and Co(II) triketonates, we predicted that a binuclear iron(III) triketonate should form which would contain two iron ions each having approximately octahedral symmetry. This can be achieved by placing three ligands around the two ions or by completing the six sites with two solvent molecules per iron and two counterions or one solvent molecule and one anion to balance the charge per ion. The analysis would indicate that a complex with two solvent molecules and two anions attached was formed. Using chloride salts of either Fe(II) or

Fe(III) in the presence of base and open to the air produced identical products. This is reasonable since Fe(II) should not be stabilized under the oxidizing conditions. We saw no evidence for a chloride ion binding in any way to the system; rather our evidence indicated binding only for the hydroxide ion. However, with use of other anions such as I^-, SO_4^{2-}, NO_3^-, and ClO_4^- in a basic solution, the resultant analyses seemed to indicate that a random mixture of anions is present. We have not characterized any of these products at the present time. Another consideration that needs to be made is the possibility of oxo bridges: two solvent molecules and two oxo bridges per molecule. The presence of linear oxo bridges between two binuclear molecules would require that two molecules be in quite close proximity. The infrared mode that is often used to characterize the linear oxo bridge in Fe(III) complexes at 820–840 cm^{-1} is not present in the IR spectrum; therefore it appears as if only the intermolecular

$$
\begin{array}{c}
\quad O \\
/ \;\; \backslash \\
Fe \quad\; Fe \\
\backslash \;\; / \\
\quad O
\end{array}
$$

bridge is present and not a linear intramolecular bridge. Analysis, then, would indicate that the molecules formed are monomeric and that the OH^- ion is the anion that is attached. Neither of the two complexes was volatile enough to get the molecular ion peak by mass spectrometry, however, so the exact molecular weight is not known, and crystals have not yet been prepared for a crystal structure to be done.

With the assumption of octahedral symmetry and a high-spin d^5 state for each iron(III), the low intensity of the electronic spectra can be explained by the fact that the ions have a symmetric $^6A_{1g}$ spectroscopic ground term. The CT band position will vary depending upon the nature of the ligand. Since these bands are due to ligand-to-metal transfers, the ability of the ligands to donate an electron should determine the position of the band. The phenyl group can facilitate the release of an electron easier than a methyl group; therefore the complex containing two phenyl groups should require less energy and appear at a longer wavelength. This is observed. The position of the CT bands relative to those of the corresponding CT bands of the diketonates was observed. The CT band appears at 392 nm for the H$_2$DBA complex whereas it appears at 333 nm[10] for the corresponding monomeric diketonate Fe(DBM)$_3$. For H$_2$BAA the CT band appears at 370 nm whereas it appears at 300 nm in the corresponding diketonate. These bathochromic spectral shifts are apparently similar to those of conjugated systems of organic molecules and may be only due to the extended conjugation in the ligand system. Another possibility, however, was proposed by Dunn[11] and considered the interaction between the metal atoms. Using the magnetic data as a guide for the strength of the metal–metal superexchange interaction, one can see how the electron exchange can cause a shift in the electronic spectral peaks by extending the conjugated system also.

The room-temperature effective magnetic moment for each of the compounds is somewhat lower than the 5.2–6.0 μ_B expected for a Fe(III) complex. This information, along with the fact that μ_{eff} for each compound decreases with decreasing temperature (Figure 1), is evidence for antiferromagnetic exchange interactions in the binuclear complexes. The extent of interaction can be observed by calculating a J value, the intradimer exchange parameter, for a d^5-d^5 binuclear system. Model compounds with a
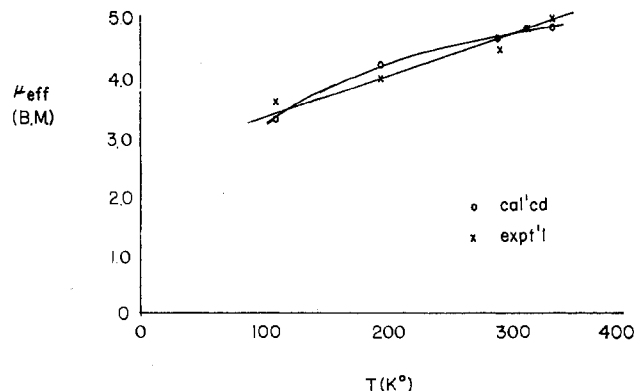
$$
\begin{array}{c}
\quad O \\
/ \;\; \backslash \\
Fe \quad\; Fe \\
\backslash \;\; / \\
\quad O
\end{array}
$$

Figure 1. Observed and calculated μ_{eff} vs. T for Fe$_2$(DBA)$_2$-(H$_2$O)$_2$(OH)$_2$.

structure (100° M–O–M angle) usually have $J \simeq -10$ cm^{-1} whereas those compounds containing a Fe–O–Fe linear bridge usually have a J value around -100 cm^{-1}.[1,12] The experimental data presented in this paper agree with those of other complexes which have a

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\quad O \\
/ \;\; \backslash \\
Fe \quad\; Fe \\
\backslash \;\; / \\
\quad O
\end{array}
$$

bridged d^5-d^5 high-spin system. However, all of the theoretically calculated susceptibilities above ~100 K lie higher than those experimentally determined. It also appears as if the susceptibility will not rise substantially with decreasing temperature and may, in fact, at some point, decrease with decreasing temperature as has been reported by other workers.[13] Reports have shown that the presence of high-spin Fe(III) impurities can influence the calculation of J and that the amount of impurities can be evaluated by measuring the magnetic susceptibility to temperatures at or near 4.2 K.[14] We have not been able to report susceptibility at those temperatures; consequently these corrections cannot be made at present, and a better fit of experimental and theoretical data is not possible.

Further work on metal(III) complexes of triketones is being carried out in this laboratory. We are attempting to prepare crystals for X-ray analysis of Fe(III) complexes with other anions, Fe(III) complexes with the Schiff-base derivatives, and the analogous Cr(III) complexes for study of the role of π bonding.

Registry No. Fe$_2$(DBA)$_2$(H$_2$O)$_2$(OH)$_2$, 68238-11-9; Fe$_2$-(BAA)$_2$(H$_2$O)$_2$(OH)$_2$, 68238-12-0.

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