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Structure and Bonding of a Compound Containing Two Quadruply Bonded Rhenium(II) Atoms. Solution of an Unusual Form of Crystallographic Disorder

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A stable compound with the formula $Re_2Cl_4(PEt_3)_4$, which can be prepared by reaction of PEt_3 with either Re_3Cl_9 or salts of the $Re_2Cl_8^{2-}$ ion, has been characterized by x-ray crystallography. It is found to have a molecular structure with the following important features. (1) It consists of *trans*-$ReCl_2(PEt_3)_2$ halves joined by a Re–Re bond. (2) The halves are in an eclipsed rotational relationship about the Re–Re bond. (3) The molecule therefore has virtual symmetry which corresponds to point group D_{2d}. (4) The Re–Re bond length is 2.232 (5) Å, which differs insignificantly from the Re–Re bond lengths in $Re_2Cl_8^{2-}$ (2.222 (2) Å) and $Re_2Cl_6(PEt_3)_2$ (2.222 (3) Å), compounds of rhenium(III) in which there are quadruple bonds between the rhenium atoms. The compound crystallizes in space group $Im3m$ with a = 12.345 (4) Å and Z = 2. The crystal structure analysis posed a nonroutine problem because of disorder. Two formula units in the cubic space group $Im3m$ would have to lie at the special positions 0, 0, 0, and $^1/_2$, $^1/_2$, $^1/_2$ and have crystallographic symmetry $m3m$, a requirement obviously inconsistent with the stoichiometry for an ordered structure. The mode of disordering was deduced to be that in which the dumbbell-shaped Re_2 units are randomly oriented along the x, y, and z axes, thus defining an apparently octahedral set of metal atoms. The Cl and P atoms are then randomly disordered over the centers of the octahedral faces. Anisotropic refinement (110 reflections with $|F_o| > 3\sigma(F_o)$) of the $^1/_3$ Re, $^1/_2$ Cl, $^1/_2$ P, and $^1/_2$ C atoms converged to residuals of R_1 = 0.041 and R_2 = 0.052, with the error in an observation of unit weight equal to 1.22 and the greatest parameter shift in the final least-squares cycle equal to 5% of its esd. It is suggested that occupation of the δ^* orbital in this sterically crowded molecule is unlikely in view of the similarity of the Re–Re bond length to those in species where the δ^* orbital is recognized to be unoccupied.

Introduction

It is well established that dinuclear rhenium(III) species contain Re–Re quadruple bonds.[2,3] In addition, structurally and electronically similar compounds are formed by technetium,[4] ruthenium,[5] tungsten,[6] chromium,[7] and, especially, molybdenum.[8] On the basis of the available qualitative descriptions of the electronic structures of such compounds only tentative predictions can be made as to their redox behavior. Recently, the scattered-wave Xα method has been used to calculate ground-state electronic structures and optical spectra for octachlorodimolybdate(II),[9] tetraformatodimolybdate(II),[10] and octachlorodirhenate(III).[11] It is not certain whether one may safely predict the electronic structures of reduction products simply by adding one or two electrons to the LUMO's of these species. Such a procedure would result in the population of the δ^* orbital by one or two electrons. This, in turn, should partially or totally nullify the δ bond and thus abolish whatever structural features are attributable solely to the presence of the δ bond.

In an effort to devise experimental tests of proposed orbital energy level diagrams, we have undertaken the preparation, isolation, and structural characterization of substances in which there should be one or two electrons in excess of the number required for the formation of the quadruple bond between the metal atoms. In this paper we deal with the structure, and its implications, of a relatively simple, symmetrical molecule containing two electrons outside of the $\sigma^2\pi^4\delta^2$ configuration which constitutes the quadruple bond, namely, $Re_2Cl_4(PEt_3)_4$. A preliminary report of this structure has appeared.[12]

Experimental Section

The compound was prepared in crystalline form in the manner previously described.[13]

Collection of X-Ray Data. A black crystal of dimensions 0.39 × 0.20 × 0.17 mm was mounted on a glass fiber and used for data collection. Preliminary work on the diffractometer indicated that the crystal system was body-centered cubic with a = 12.345 (4) Å. The cell constant and the orientation matrix for data collection were obtained from least-squares refinement of 15 reflections in the range 14° < 2θ (Mo Kα) < 27°. Additional crystal data are given in Table I. The observed density was measured by flotation in a mixture of diethyl ether and 1,4-diiodobutane. The width at half-height from ω scans of several intense reflections was 0.2°.

Table I. Data for $Re_2Cl_4[P(C_2H_5)_3]_4$

$C_{24}H_{60}Cl_4P_4Re_2$
Fw 986.86
$a = 12.345$ (4) Å
$V = 1881$ (1) Å^3
$Z = 2$
$d_{calcd} = 1.742$ g cm^{-3}
$d_{obsd} = 1.75 \pm 0.02$ g cm^{-3} (by flotation)
Cubic, body centered
$Im3m$-O_h^9 (No. 229)
Mo Kα radiation
$\mu = 72.7$ cm^{-1}

Data were collected at 20 ± 2° on a Syntex $P\bar{1}$ diffractometer using Mo Kα radiation and a graphite-crystal monochromator in the incident beam. A total of 608 nonunique reflections in the range $0 < 2\theta \leq 50°$ were measured using the θ–2θ scan technique with a range of 0.7° below the Kα_1 peak to 0.7° above the Kα_2 peak and with a scan rate varying from 4 to 24°/min depending on the intensity of the reflection. No significant change in intensity was observed for four standard reflections measured every 50 reflections throughout the data set. Additional details of data collection have been given previously.[14]

In data reduction[15] the factor p used in calculating standard deviations was initially set at 0.05.[15] A numerical absorption correction was applied to the data; the transmission factors ranged from 0.307 to 0.370 with an average of 0.355. An extinction correction was not necessary.

Solution and Refinement of Structure. The only extinction observed in the data was that expected for the body-centering condition. Thus the centric space groups $Im3$ and $Im3m$ and the noncentric space groups $I23$, $I2_13$, $I432$, and $I43m$ are each consistent with the extinctions. Refinement was begun in space group $Im3$ and then a change was made to $Im3m$ after the location of carbon atoms suggested that the higher symmetry space group was more appropriate; vide infra.

The limitation of two molecules per unit cell requires the molecular unit to be located on the origin and imposes $m3$ or $m3m$ symmetry on the molecule. This clearly suggests that the crystal is disordered. A three-dimensional Patterson function showed heavy atoms in 12-fold degenerate positions (12d in $Im3$ or 12e in $Im3m$) and in the 16-fold degenerate position (16f). The 12-fold positions describe octahedra centered at (0, 0, 0) and ($^1/_2$, $^1/_2$, $^1/_2$); the 16-fold positions lie on the C_3 axes and are centered above each of the eight faces of each octahedron. The distance along an edge of the octahedron was 1.55 Å, while the distance between vertices lying on the same C_4 axis was 2.22 Å, as determined from the Patterson map. The shortest distance from a vertex to the heavy atom on the C_3 axis was 2.68 Å.

A logical explanation for this result is the following. The two Re atoms of an individual $Re_2Cl_4[P(C_2H_5)_3]_2$ molecule lie on one of the

Table II. Positional Parameters, Anisotropic Thermal Parameters, and Root-Mean-Square Amplitudes of Thermal Vibration[a]

Atom	$x = y$	z	$\beta_{11} = \beta_{22}$	β_{33}	β_{12}	$\beta_{13} = \beta_{23}$	Rms amplitudes, Å Min	Intermed	Max
Re (12e)	0.0904 (2)	x	87 (2)	β_{11}	0	0	0.259 (3)	0.261 (3)	0.261 (3)
Cl (16f)	0.1317 (18)	x	216 (24)	β_{11}	−54 (13)	β_{12}	0.29 (4)	0.46 (2)	0.46 (2)
P (16f)	0.1403 (15)	x	105 (9)	β_{11}	−30 (6)	β_{12}	0.19 (2)	0.32 (1)	0.32 (1)
C(1) (48k)	0.1016 (27)	0.2852 (35)	327 (40)	179 (38)	−47 (63)	−9 (30)	0.37 (4)	0.47 (5)	0.54 (5)
C(2) (48k)	0.1558 (30)	0.3670 (37)	427 (52)	231 (52)	−30 (76)	−115 (42)	0.32 (5)	0.59 (6)	0.62 (6)

[a] Numbers in parentheses in this and other tables are the estimated standard deviations in the least significant digits. The form of the thermal ellipsoid is $\exp[-10^4(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$.

C_4 axes of the octahedron, giving a reasonable Re–Re bond length of ca. 2.22 Å. The Cl and P atoms lie in the 16f positions, giving Re–Cl and Re–P distances of ca. 2.68 Å. In one-third of the unit cells the Re–Re bond lies along the C_4 axis parallel to the x axis; in another third of the unit cells the Re–Re bond lies along the C_4 axis parallel to the y axis; and in the remaining third of the cells the bond is parallel to the z axis. The overall result of this disorder is that each 12e position (12d in $Im3$) has an occupancy factor of $^1/_3$ for Re and each 16f position has an occupancy factor of $^1/_2$ for Cl and $^1/_2$ for P. This model was refined in four full-matrix least-squares cycles using isotropic thermal parameters and an average scattering factor ($^1/_2$ Cl plus $^1/_2$ P) for the 16f positions. The resulting agreement factors were

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.122$$

and

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/w|F_o|^2]^{1/2} = 0.178$$

Anisotropic refinement (eight variables) reduced R_1 and R_2 to 0.101 and 0.163, respectively.

At this point a successful attempt to separate the Cl and P positions was made. Starting with a model in which the Cl and P positions were separated by the expected differences in the Re–Cl and Re–P bond lengths, the Cl and Re positions and temperature parameters were refined in one least-squares cycle. This was followed by a cycle in which the P and Re positions were refined and the Cl positions were held constant. This process was repeated until each parameter shift was less than the esd of the parameter. Then all three atoms were refined together in several cycles which converged to R_1 of 0.091 and R_2 of 0.146.

At this point a difference Fourier synthesis was computed, which revealed the positions of the ethyl C atoms at 0.093, 0.093, 0.279 and 0.145, 0.145, 0.361. Such an x, x, z position corresponds to one of the 48k positions in $Im3m$; therefore refinement was continued in this space group.

An absorption correction was made and the equivalent forms hkl, hlk, and klh were averaged since all three had been collected. This gave a unique data set of 198 reflections, of which 110 reflections with $|F_o| > 3\sigma(F_o)$ were used in least-squares refinement. Plots of $\sum w|F_o - F_c|$ vs. $|F_o|$ for various values of the factor p, used in calculating $\sigma(F_o{}^2)$, showed that the best value for p was 0.06. Using this value, least-squares refinement gave $R_1 = 0.055$ and $R_2 = 0.071$. However, several features were disturbing: (1) no number of least-squares cycles could reduce the parameter shifts to less than 0.7 times their esd's, (2) the thermal parameters for the atoms were uncharacteristically anisotropic, (3) the error in an observation of unit weight was high (1.68). The apparent cause of these anomalies was the 222 reflection for which $|F_o - F_c|/\sigma(F_o)$ was 8.7. Rejection of this reflection reduced the agreement factors to 0.041 and 0.052, respectively. The error in an observation of unit weight was reduced to 1.22 and the thermal parameters assumed normal values. The greatest parameter shift in the last cycle of least squares was 0.05 times its esd. A final difference Fourier map showed residual electron density of 0.89 e Å^{-3} at (0, 0, 0), the center of the Re–Re bond; the height of this peak is approximately twice as high as that found for the half-carbon atoms in a previous map. All other peaks were less than 0.31 e Å^{-3}.

Scattering factors were taken from Cromer and Waber.[16] Anomalous dispersion factors for Re, Cl, and P atoms were those of Cromer and Liberman.[17] The function minimized in least-squares refinements was $\sum w||F_o| - |F_c||^2$ where the weight w is given by $4F_o{}^2/\sigma^2(F_o{}^2)$.

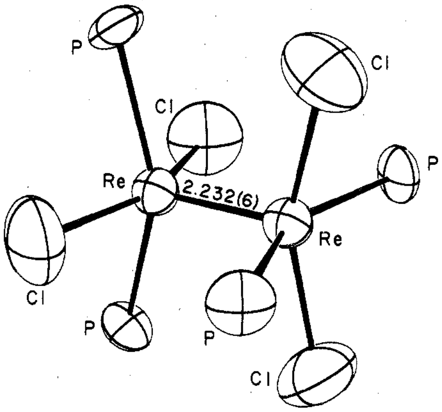

Figure 1. The central $Re_2Cl_4P_4$ skeleton of the $Re_2Cl_4(PEt_3)_4$ molecule. The ethyl groups have been omitted for clarity.

Table III. Bond Distances (Å) and Bond Angles (deg) for $Re_2Cl_4[P(C_2H_5)_3]_4$

	Distances		
Re–Re	2.232 (6)	P–C(1)	1.91 (4)
Re–Cl	2.36 (4)	C(1)–C(2)	1.38 (5)
Re–P	2.53 (3)		
	Angles		
Re′–Re–Cl	102.5 (4)	Re–P–C(1)	114 (2)
Re′–Re–P	104.1 (3)	Re–P–C(1)′	83 (2)
Cl′–Re–Cl	155.0 (7)	C(1)′–P–C(1)	114 (1)
Cl–Re–P	153.4 (2)	P–C(1)–C(2)	116 (4)
P′–Re–P	151.7 (5)		

A list of structure factor amplitudes in the form of $10|F_o|$ and $10|F_c|$ in electrons is available as supplementary material. Positional and anisotropic thermal parameters are tabulated in Table II.

Results

The molecular structure is shown in Figure 1. The atomic positional and thermal parameters are listed in Table II and the molecular dimensions are listed in Table III. The manner in which the molecules are disordered on sites of $m3m$ symmetry is unique but, at the same time, not unrelated to the type of disordering which has been found in $K_4Mo_2Cl_8 \cdot 2H_2O$[18] and $[(C_4H_9)_4N]_2Re_2Cl_8$.[19] In these cases, a fraction of the nearly cubic M_2Cl_8 anions are tipped 90° to the major orientation. This is possible because the nearly cubic array of Cl atoms must interact with its surroundings in a manner almost independent of the orientation of the pair of metal atoms inside of it. In the present case, the more bulky PEt_3 groups shield the Re_2 core so effectively from the surroundings that a completely isotropic disorder is energetically possible.

Because of the disorder, some of the molecular dimensions are measured with less accuracy than might otherwise have been expected. However, the precision in the measurements of the Re–Re, Re–Cl, and Re–P distances is good and the results provide a valid basis for discussing how molecular structure and electronic structure are related in this and similar molecules.

Table IV. Comparison of Bond Lengths in Three Dirhenium Species

	$Re_2Cl_4(PEt_3)_4$	$Re_2Cl_6(PEt_3)_2$	$Re_2Cl_8^{2-}$
Re–Re	2.232 (6)	2.222 (3)	2.222 (2)
Re–Cl	2.36 (4)	2.31 ± 0.03	2.32 ± 0.01
Re–P	2.53 (3)	2.449 (6)	

Discussion

There are a number of ways to approach the question of what happens when additional electrons are added to dinuclear systems in which there are present precisely the number of electrons necessary to form eight metal–ligand bonds and a quadruple bond between the metal atoms. Solution studies involving electrochemical reduction, often coupled with an EPR study of those species with an unpaired electron, provide certain types of information; for example, they can provide valuable information on stabilities when the technique of cyclic voltammetry is employed. Several such studies have recently been reported.[20,21]

Another approach is the structural one, in which the effect of adding one or more electrons upon bond lengths or other structural features is examined. It is assumed that if a certain bond—or set of equivalent bonds—is lengthened by the addition of electrons, this must indicate that the electrons enter an orbital which is antibonding with respect to that particular bond, or set of bonds. Obviously, this approach is most powerful and unambiguous when the reduced species has precisely the same composition and qualitatively the same structure as the molecule with which it is to be compared. In practice, however, some deviation from this ideal must usually be tolerated, and the possible effects of variations other than the mere addition of an electron or two must be kept in mind.

In the present instance, the comparison we wish to make is between the structure of $Re_2Cl_4(PEt_3)_4$, which is reported in this paper, and those of the $Re_2Cl_8^{2-}$ ion and the $Re_2Cl_6(PEt_3)_2$ molecule which have previously been described.[19,22] In each case the molecule has an eclipsed configuration. The bond lengths are compared in Table IV. It is clear that there is no difference among the three Re–Re bond distances which is significant in either a statistical or a stereochemical sense. It appears that metal–ligand distances in $Re_2Cl_4(PEt_3)_4$ may be greater, by about 0.04 and 0.08 Å for Re–Cl and Re–P, respectively, than those in the other species. It is true that the apparent increase in the Re–Cl distance cannot be considered statistically significant. Thus, in summary, the presence of two additional electrons in $Re_2Cl_4(PEt_3)_4$, as compared to $Re_2Cl_8^{2-}$ and $Re_2Cl_6(PEt_3)_2$, does not affect the structure qualitatively, does not significantly affect the Re–Re bond length, but does perhaps slightly weaken the metal–ligand bonds.

We must now ask what conclusions, if any, can be drawn concerning the bonding from the structural effects just mentioned. First, it should be noted that the retention of the eclipsed configuration in $Re_2Cl_4(PEt_3)_4$ cannot be taken as evidence for or against the retention of the δ component of the metal-to-metal bond, because steric factors alone could serve to stabilize the observed rotational conformation. The staggering of the large PEt_3 groups with respect to one another results in eclipsing of the ligand set as a whole.

The second observation, the lack of any significant increase in the Re–Re distance, does seem to us to carry a very clear implication with regard to electronic structure. Since the presence of four PEt_3 ligands in place of smaller Cl^- ligands should increase the steric forces tending to stretch the Re–Re bond, any decrease in the strength of that bond should surely result in an increase in the Re–Re distance. We conclude that the two additional electrons in $Re_2Cl_4(PEt_3)_4$, as compared with $Re_2Cl_8^{2-}$ and $Re_2Cl_6(PEt_3)_2$, cannot occupy an orbital that is antibonding with regard to the Re–Re bond.

The recently published SCF–Xα–muffin tin calculation[11] on $Re_2Cl_8^{2-}$ (and also the one[9] for isoelectronic $Mo_2Cl_8^{4-}$) indicates that the lowest empty orbital is the b_{1u} or δ^* orbital. From this, it might be tempting to assume that in $Re_2Cl_4(PEt_3)_4$ two electrons should occupy this orbital. This, however, should lengthen the Re–Re bond, since the δ contribution would be approximately nullified. On the basis of previous results[21] on the $Mo_2(SO_4)_4^{3-,4-}$ species, where the δ bond order changes by 0.5 and the Mo–Mo bond distance increases by 0.05 Å, and by comparing the Re–Re distance (2.293 Å) in $Re_2Cl_5(CH_3SCH_2CH_2SCH_3)_2$, where there is a triple bond,[23] with those in $Re_2Cl_8^{2-}$ and $Re_2Cl_6(PEt_3)_2$ (Table IV), an increase in the range of 0.06–0.10 Å might be expected if the δ^* orbital were to become doubly occupied.

Finally, if the added pair of electrons does not populate the δ^* orbital, it is necessary to suggest an alternative location. In view of the fact that the metal–ligand bonds appear to be slightly lengthened, though this is not a marked effect, and may even be illusory, it could be that the added electrons occupy some orbital which is more or less antibonding with respect to the metal–ligand linkages. Some of the lower unfilled orbitals do have this character, but the occupation of such an orbital is not the obvious prediction from the published energy level diagram.[11]

On the basis of the principle that added electrons should occupy those regions of space where there is the least electron density already present, one might consider the regions at each end of the molecule along the extensions of the Re–Re axis. These are the regions of the σ-nonbonding orbitals that were postulated to exist in the original, qualitative description of the quadruply bonded species.[2] If the d_{z^2} orbital is assumed to be completely engaged in the metal-to-metal σ bond, then the provenence of such a molecular orbital would have to be in the 6s and/or 6p atomic orbitals of the rhenium atoms.[24] While these atomic orbitals are of appreciably higher energy than the metal 5d orbitals and no such σ molecular orbital is found at low energy in the Xα calculation,[11] it may be that when the two additional electrons are actually present, such an orbital becomes more stable. Against this is the ESR spectrum[20] of $Tc_2Cl_8^{3-}$, where the g values appear more consistent with the presence of a δ^* electron than a σ electron; the arguments on this point are not conclusive, however. EPR data[20] for the $Re_2Cl_4(PEt_3)_4^+$ ion were fragmentary and entirely inconclusive.

The problem of what orbital is occupied by the two "additional" electrons in $Re_2Cl_4(PEt_3)_4$ remains unsolved. However, the structural results do seem to show one thing, namely, that these electrons do not occupy the δ^* orbital. This is not necessarily inconsistent with the results of the Xα calculations on $Re_2Cl_8^{2-}$ and $Mo_2Cl_8^{4-}$, but neither is it readily explained by those MO treatments.

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Supplementary Material Available: Listing of structure factor amplitudes (1 page). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Magnetism of Polynuclear Chelates. Structural and Magnetic Comparison of In-Plane and Out-of-Plane Exchange in Three Polynuclear Copper Complexes

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Three related Cu(II) complexes were prepared from 1,3,5-triketonate-type ligands and their structures determined by single-crystal x-ray techniques. The complexes are $Cu_2(BAA)_2(py)_2$, containing the ligand 1-phenyl-1,3,5-hexanetrionate dianion, $[Cu_2(DTFACP)_2(H_2O)_2]_2$, containing the dianion of 2,5-bis(trifluoroacetyl)cyclopentanone, and $[CuH_2(BAA)_2en]_2$, containing the dianion of *N,N'*-bis(benzoylacetylacetone)ethylenediamine. The results show that $Cu_2(BAA)_2(py)_2$ is a binuclear monomer with each of the two copper atoms coordinated to four equatorial ketonic oxygens and one pyridine in typical five-coordinate manner: *Pbca*, $a = 8.473$ (3) Å, $b = 25.377$ (15) Å, $c = 19.000$ (10) Å, $Z = 4$, $R = 0.061$. The complex $[Cu_2(DTFACP)_2(H_2O)_2]_2$ is a dimer of binuclear molecules in which each copper atom is bonded to four equatorial ketonic oxygens and one axial H_2O (2.31 Å): *Pbca*, $a = 10.721$ (10) Å, $b = 24.634$ (10) Å, $c = 17.739$ (16) Å, $Z = 8$, $R = 0.066$. The complex $[CuH_2(BAA)_2en]_2$ is a mononuclear dimer in which the copper atom is bonded to four equatorial ketonic oxygens and an axial oxygen from the adjacent molecule (2.60 Å): $P2_1/c$, $a = 10.745$ (2) Å, $b = 9.205$ (2) Å, $c = 23.388$ Å, $\beta = 100.04$ (2)°, $Z = 4$, $R = 0.056$. The magnetic exchange pathways possible in the complexes are as follows: $Cu_2(BAA)_2(py)_2$, in-plane exchange; $[Cu_2(DTFACP)_2(H_2O)_2]_2$, both in-plane and out-of-plane exchange; $[CuH_2(BAA)_2en]_2$, out-of-plane exchange. The similarities between the magnetic properties of $Cu_2(BAA)_2(py)_2$ and $[Cu_2(DTFACP)_2(H_2O)_2]_2$ suggest only negligible out-of-plane exchange in the latter compound. Both of these compounds exhibit strong antiferromagnetism with exchange constants, J, of about -370 cm^{-1}. The validity of ignoring the out-of-plane exchange is supported by the normal magnetic behavior of $[CuH_2(BAA)_2en]_2$ down to 10 K.

Introduction

The β-polyketonates are an interesting and versatile class of ligands, especially when considered as a homologous series in which the 1,3-diketonates are the simplest members. In all probability, the higher homologues have coordinating ability similar to that of the 1,3-diketonates with the added dimension of being able to chelate more than one metal ion within the same molecule. The subject of a continuing program in our laboratory is the structure and magnetic superexchange in multinuclear chelates of β-polyketonates. These ligands offer a singularly attractive opportunity to investigate superexchange between several different metal ions in very similar ligand environments. Under such conditions, magnetic exchange is largely determined by the symmetry of the exchanging electrons which in turn is determined by the ligand field symmetry. Our immediate goals are (1) to characterize the magnetic properties of the possible binuclear complexes with electronic configurations d^1–d^1 through d^9–d^9 and (2) to gather enough structural data to allow a general discussion of structural characteristics as they pertain to magnetic exchange. To date, the studies have included structural and magnetic results on 1,3,5-triketonates and their Schiff base derivatives: d^7–d^7 (Co^{2+}–Co^{2+}),[1] d^8–d^8 (Ni^{2+}–Ni^{2+}),[2] d^9–d^9 (Cu^{2+}–Cu^{2+}),[3] d^8–d^{10} (Ni^{2+}–Zn^{2+}),[4] and d^8–d^1 (Ni^{2+}–VO^{2+}).[5] In addition, magnetic studies have been carried out on d^1–d^1 (VO^{2+}–VO^{2+})[6] and d^3–d^3 (Cr^{3+}–Cr^{3+})[7] complexes. Many of the structural and magnetic data have been reviewed by Glick and Lintvedt.[7] The present work is concerned with the