is of the utmost importance in tritiation reactions, especially to high specific activities, since degradation of the organic substrate through exposure to high tritium β radiation fields must be minimized. Thus, the present catalytic method should offer significant advantages over other radiation-induced[5,6] and catalytic procedures[7] for tritium labeling because of its simplicity, speed, selectivity for aromatic protons, and freedom from side reactions.

A plausible mechanism for the labeling reaction would involve the formation of a complex between the catalyst and the organic compound, possibly through a π-associative type species as proposed for other catalytic exchange systems.[8,9] Hydrolysis of the complex with tritiated water could be accompanied by a proton transfer resulting in incorporation of tritium into the organic substrate.

Acknowledgment. We thank the Australian Research Grants Committee and the Australian Institute of Nuclear Science and Engineering for the support of the research at The University of New South Wales.

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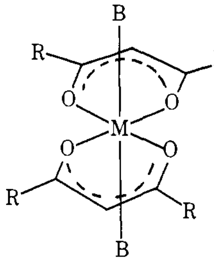
Copper(II), Nickel(II), and Cobalt(II) Chelates of 1,3,5,7-Tetraketonates. Characterization and Preliminary Magnetic Studies on Bi- and Trinuclear Chelates

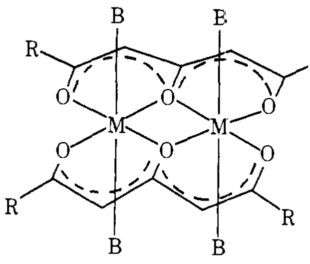
Sir:

In the study of magnetic exchange phenomena in polynuclear metal clusters it would be desirable to be able to investigate homologous series of complexes in which the members of the series contain one, two, three, etc., metal ions. If the metal ions in each member of these series were in similar chemical environments, then the effect of exchange over varying numbers of metal centers could be critically assessed. A class of ligands we call the polyketones is capable of producing series of this type. The generalized structure for the first three members is shown below. In the series shown M is a divalent metal ion and B is a neutral ligand such as H_2O or pyridine. When M is Cu(II), the adduct ligands may or may not be present. However, when present no more than one per Cu(II) is normally found.

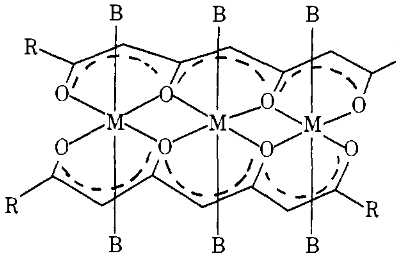
The first member, the 1,3-diketonates, needs no further comment here. The second member, the 1,3,5-triketonates, has received very little attention. To date only dicopper(II) bis(1,3,5-triketonato) type complexes have been reported[1-3] although Ni(II),[4] Co(II),[5] Fe(II),[6] Mn(II),[6] and Cr(III)[6] chelates have been prepared and their magnetic properties studied in a preliminary manner. To our knowledge, no examples of the third member of the series, the 1,3,5,7-tetraketonates, have been reported. We wish to report at this time the first chelates of this type.



1,3-diketonates



1,3,5-triketonates



1,3,5,7-tetraketonates

The tetraketonate complexes prepared contain the ligand 1,7-diphenyl-1,3,5,7-heptanetetraone. The ligand itself was first reported by Miles, Harris, and Hauser[7] who prepared it by the benzoylation of (1) acetylacetone and (2) 1-phenyl-1,3,5-hexanetrione. In our hands, method 2 was far more successful. Adopting the commonly used nomenclature of the 1,3-diketones, the trivial name for this ligand is dibenzoylacetylacetone. Henceforth, we will use the abbreviation H_3DBAA for the completely protonated molecule. The preparation of H_3DBAA involves a straightforward Claisen condensation using NaH as the base and monoglyme as the solvent. The golden, plate-like crystals melt at 91–93°. *Anal.* Calcd for $C_{19}H_{16}O_4$: C, 74.02; H, 5.22. Found: C, 74.15; H, 5.16. The molecule contains three enolizable protons and may function as a mono-, di-, or trianionic ligand, H_2DBBA^-, $HDBAA^{2-}$, and $DBAA^{3-}$.

Chelates were prepared in a variety of ways. The most successful methods used a 1.0:0.67 molar ratio of metal ion to H_3DBAA in $MeOH-H_2O$ or acetone–H_2O solvent systems. Either NaOH or $NaC_2H_3O_2$ was added as a base. All of the chelates precipitated as powders that are relatively insoluble in common organic solvents and H_2O. They are soluble in coordinating solvents such as pyridine. Isolation of complexes with two or three metal ions appears to depend upon preparative details such as the solvent, temperature, and base used. The chelates were washed with H_2O, and for Ni(II) and Cu(II) complexes with dilute

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NH_4OH, to remove unreacted metal salts. They were then washed with methanol and acetone to remove unreacted ligand. The compounds were dried in a vacuum desiccator over $CaCl_2$, ground, and soxhleted with acetone and/or methanol for 2 or 3 days until clear.

Anal. Calcd for $Cu_2(C_{19}H_{14}O_4)_2 \cdot H_2O$: C, 60.72; H, 3.73; Cu, 16.91. Found: C, 60.85; H, 3.70; Cu, 16.51. Calcd for $Cu_3(C_{19}H_{13}O_4)_2(H_2O)_3$: C, 53.61; H, 3.76; Cu, 22.40. Found: C, 53.44; H, 3.80; Cu, 22.51. Calcd for $Ni_2(C_{19}H_{14}O_4)_2(H_2O)_4 \cdot H_2O$: C, 55.65; H, 4.76; Ni, 14.32. Found: C, 55.44; H, 4.65; Ni, 14.15. Calcd for $Ni_3(C_{19}H_{13}O_4)_2(H_2O)_6$: C, 50.99; H, 4.28; Ni, 19.69. Found: C, 50.35; H, 4.41; Ni, 19.80. Calcd for $Co_3(C_{19}H_{13}O_4)_2(H_2O)_6$: C, 50.95; H, 4.25; Co, 19.70. Found: C, 51.11; H, 4.22; Co, 19.13.

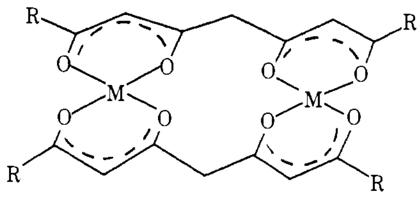
The infrared spectra of these compounds are all very similar. None of the spectra exhibit absorptions due to free, unchelated carbonyl groups. Even the compounds containing only two metal ions do not contain "free carbonyls" as evidenced by their infrared spectra.

Preliminary magnetic susceptibility measurements between 77 and 300°K have uncovered several interesting features (Table I). For example, the moment of $Cu_3(DBAA)_2(H_2O)_3$ is unusually low indicating inter- as well as intramolecular exchange, the high moments for $Ni_3(DBAA)_2(H_2O)_6$ are perhaps due to quite strong ferromagnetic exchange, and the temperature dependence of the $Co_3(DBAA)_2(H_2O)_6$ magnetic moments are indicative of reasonably strong antiferromagnetism. All of these features are under more detailed study.

Table I. Magnetic Moments (BM) Reported on a Per Metal Basis

	300°K	276°K	195°K	77°K
$Co_3(DBAA)_2(H_2O)_6$	4.71		4.66	4.09
$Cu_3(DBAA)_2(H_2O)_3$	0.90	0.82	0.63	0.49
$Cu_2(HDBAA)_2 \cdot H_2O$	1.89	1.80	1.78	1.63
$Ni_3(DBAA)_2(H_2O)_6$	3.95	3.74	3.52	3.35
$Ni_2(HDBAA)_2(H_2O)_4 \cdot H_2O$	3.14		3.08	2.88

While structural data for these complexes have not yet been obtained, certain aspects seem clear from the magnetic data and by analogy to the structure of the 1,3,5-triketonates. First, it is most probable that the $DBAA^{3-}$ ligand is planar due to the presence of sp^2 hybridized carbons. The planarity of coordinated 1,3,5-triketonates has been established by a single-crystal X-ray structure determination of bis(1,5-diphenyl-1,3,5-pentanetrionato)tetra(pyridine)dicobalt(II).[5] Indeed, the two Co atoms and the six oxygens are coplanar within experimental error. It is reasonable that these structural features be carried over to the tetraketonates as well. Second, the complexes with only two metal ions appear to have the metals separated rather than adjacent to one another. This conclusion is supported by the lack of "free carbonyl" absorptions in the infrared spectra and the nearly normal room temperature magnetic moments. Thus, of the three probable structures shown below, **1** or **2** seem most reasonable. (Note: H_2O has been omitted for simplicity.) The somewhat depressed magnetic moments of the binuclear complexes at 77°K may be due to exchange through the bridging ligand systems of **1** and **2**. It is clear, however, that if the metals were in the environment shown in **3** much different magnetic behavior would be expected. Since the magnetic behavior is not at all similar to analogous 1,3,5-triketonates[2–4] we have discounted **3** as a possibility. For structure **1** or **2** the interesting possibility exists that a third metal ion could be placed in the vacant site. From the standpoint of magnetic exchange studies it would be most interesting if the third metal ion were different from the original two.



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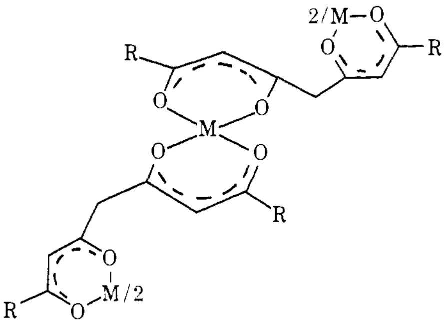

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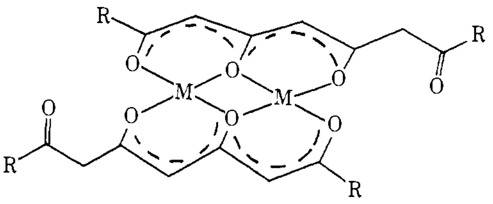

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A Novel Electrocyclic Process. Facile Generation of a Diazacyclopentadienone

Sir:

The decomposition of bisdiazo compounds as a route to strained olefins has met with limited success.[1,2] We have shown that the photochemical decomposition of 1,3-bisdiazo-1,3-diphenyl-2-propanone produces diphenylcyclopropenone as the major initial product

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