Communications

The First Definitive Evidence for a New Class of Trinuclear Metal Complexes, the 1,3,5,7-Tetraketonates. Molecular Structure of the Heterotrinuclear Complex Bis[1,7-diphenyl-1,3,5,7-heptanetetraonato(3–)]bis[dioxouranium(VI)]nickel(II) Tetrapyridine–2-Pyridine

Sir:

In this report we wish to communicate the first structural characterization of a trinuclear complex of a 1,3,5,7-tetraketonate. To our knowledge, the only previously published information on 1,3,5,7-tetraketonate complexes is contained in a brief communcation from our laboratory.[1] The compound described herein is a neutral heterotrinuclear molecule containing two essentially coplanar trianionic 1,7-diphenyl-1,3,5,7-heptanetetraonate ($DBAA^{3-}$)[2] ligands, two UO_2^{2+} ions coordinated at the terminal ligand sites (enolate oxygens 1,3 and 5,7), and one Ni(II) bound at the central site (enolate oxygens 3,5). In addition, each U atom is bonded to a pyridine N which is in the plane of the tetraketonates and the Ni atom is bound to two pyridine N atoms, one above and one below the molecular plane.

The synthetic strategy used to prepare the compound (and several others related to it) depends upon the fact that the preferred pentagonal-bipyramidal geometry of the seven-coordinate U(VI) forces the UO_2^{2+} ions to occupy terminal positions[3] in the tetraketonates. As a result of this specificity, the central position is open for a metal ion that might be 4-, 5-, or 6-coordinate. The extent of coordination specificity is emphasized by the fact that a series of $[(UO_2)_2M(DBAA)_2(solvent)_4]$ complexes, where M(II) = Zn, Cu, Ni, Co, or Mn, is readily prepared in high yield by simply reacting a stoichiometric ratio of 2:2:1 tetraketone:uranyl acetate:metal(II) acetate in methanol with $(C_2H_5)_3N$ as a base.[4] Both the ease with which three metal ions are introduced and the specificity with which the heterotrinuclear complexes are formed are quite surprising.

Crystals of $[(UO_2)_2(Ni)(DBAA)_2(py)_4]\cdot 2py$ were obtained by crystallizing the initial product from pyridine. A crystal of dimensions 0.67 × 0.20 × 0.20 mm was sealed in a capillary and studied in a Syntex P2$_1$ diffractometer with graphite-monochromated Mo Kα radiation. The compound crystallizes in the monoclinic space group $P2_1/c$ with cell parameters a = 13.436 (3) Å, b = 24.011 (6) Å, c = 10.556 (2) Å, β = 108.12 (1)°, $Z = 2$, 1.58 g/cm^3 < D_{measd} < 1.82 g/cm^3, and D_{calcd} = 1.72 g/cm^3. A total of 4262 data with $2\theta \leq 45°$ were examined, of which 2961 were used in the analysis ($I > 3\sigma(I)$). Absorption corrections (μ = 50.85 cm^{-1}) were applied to the data. The structure was solved by conventional heavy-atom techniques.[5] Full-matrix least-squares refinement with all atoms anisotropic (excepting the hydrogens and those of pyridines of crystallization) converged with discrepancy factors of R = 0.031 and R_w = 0.038 and an error of fit = 1.11. The basic structure is described above with the nickel atom occupying a crystallographic center of symmetry. The bond distances and angles in the coordination spheres of U and Ni are compiled in Table I. An ORTEP drawing of the molecule is presented in Figure 1. The thermal ellipsoids are at 50% probability.[6] The U–Ni distance is 3.5186 (7) Å.

Table I. Some Bond Lengths (Å) and Angles[b] (Deg) for the Coordination Spheres of U and Ni in $[(UO_2)_2Ni(DBAA)_2(py)_4]$[a]

U(1)–O(5)	1.756 (6)	U(1)–O(4)	2.453 (5)
U(1)–O(6)	1.763 (6)	U(1)–O(1)	2.465 (5)
U(1)–O(3)	2.247 (6)	U(1)–N(1)	2.584 (9)
U(1)–O(2)	2.252 (6)		
Ni(1)–O(1)	2.029 (5)	Ni(1)–N(2)	2.175 (6)
Ni(1)–O(4)	2.032 (5)		
O(5)–U(1)–O(6)	177.0 (3)	O(3)–U(1)–O(2)	148.7 (2)
O(5)–U(1)–O(3)	88.7 (2)	O(3)–U(1)–O(4)	71.6 (2)
O(5)–U(1)–O(2)	90.8 (3)	O(3)–U(1)–O(1)	138.8 (2)
O(5)–U(1)–O(4)	95.2 (2)	O(3)–U(1)–N(1)	73.7 (2)
O(5)–U(1)–O(1)	85.4 (2)	O(2)–U(1)–O(4)	139.5 (2)
O(5)–U(1)–N(1)	86.7 (3)	O(2)–U(1)–O(1)	72.2 (2)
O(6)–U(1)–O(3)	90.5 (3)	O(2)–U(1)–N(1)	75.1 (2)
O(6)–U(1)–O(2)	88.4 (3)	O(4)–U(1)–O(1)	68.5 (2)
O(6)–U(1)–O(4)	87.3 (2)	O(4)–U(1)–N(1)	145.1 (2)
O(6)–U(1)–O(1)	97.1 (2)	O(1)–U(1)–N(1)	146.2 (2)
O(6)–U(1)–N(1)	90.2 (3)		
O(1)–Ni(1)–O(4)	85.9 (2)	O(1)–Ni(1)–N(2′)	88.3 (2)
O(1)–Ni(1)–O(4′)	94.1 (2)	O(4)–Ni(1)–N(2)	88.6 (2)
O(1)–Ni(1)–N(2)	91.7 (2)	O(4)–Ni(1)–N(2′)	91.4 (2)

[a] The abbreviation $DBAA^{3-}$ is based on the trivial name dibenzoylacetylacetonate. [b] The primed atoms are related to the corresponding unprimed atoms by a center of symmetry.

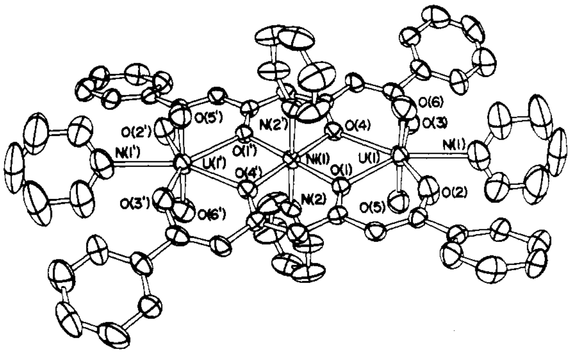
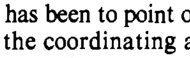


Figure 1. ORTEP drawing of $[(UO_2)_2Ni(DBAA)_2(py)_4]$.

The β-polyketones form a series of ligands for which it is possible to envision designing structurally related mono-, di-, trinuclear, etc. complexes for n = 1–3, etc. While the mononuclear 1,3-diketonates are extremely well studied, as recently as ten years ago there were very few reports of binuclear 1,3,5-triketonates. Several studies on the binuclear members of the series have been published in the past few years.[7-10] One result of these studies has been to point out that there are many similarities between the coordinating abilities of the ligands and molecular structure of the complexes for the 1,3,5-triketonates and the 1,3-diketonates. The structural results presented here clearly establish that 1,3,5,7-tetraketonates can



β-polyketonates

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(2) The ligand abbreviation H_3DBAA is based on the trivial name dibenzoylacetylactone.
(3) Lintvedt, R. L.; Ahmad, N. *Inorg. Chem.* accepted for publication.
(4) Schoenfelner, B. A.; Lintvedt, R. L., unpublished results.
(5) A description of the programs, weighting scheme, and experimental details is given in: Heeg, M. J.; Mack, J. L.; Glick, M. D.; Lintvedt, R. L. *Inorg. Chem.* **1981**, *20*, 833.
(6) Johnson, C. K. "ORTEP II", Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.
(7) Heeg, M. J.; Mack, J. L.; Glick, M. D.; Lintvedt, R. L. *Inorg. Chem.* **1981**, *20*, 833 and references therein.

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be expected to behave with respect to their coordinating ability and their structural chemistry in manners similar to the 1,3-di- and 1,3,5-triketones. Therefore, these ligands should provide a convenient entry into an extensive new class of molecular trinuclear complexes, both homo- and heterotrinuclear. This study is the first stage of a long-range project to carefully characterize and investigate the properties of the trinuclear metal complexes of the 1,3,5,7-tetraketonates and their Schiff-base derivatives. A forthcoming paper contains complete structural data for the compound described herein as well as for two other related compounds and the synthesis, magnetic properties, electrochemical results, and spectral properties for several heterotrinuclear 1,3,5,7-tetraketonates.

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Registry No. $[(UO_2)_2(Ni)(DBAA)_2(py)_4]\cdot 2py$, 81205-64-3.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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Synthesis of a Mixed-Valence Copper Complex via Free-Radical Additions to a Copper(I) Dimer

Sir:

We recently described the synthesis and structure of a compound that contains two cofacial, three-coordinate (16e) copper(I) moieties coordinated to two bridging phosphino diketonate compartmentalized ligands.[1] This complex is an unusual example of a readily isolable, coordinatively unsaturated, binuclear copper(I) complex[2] and is ideally suited for oxidative-addition studies. Oxidative additions to bimetallic complexes have received considerable attention recently although the majority of such studies have been restricted to the group 8 metals.[3] The mechanisms for such processes involve either localized (monometallic) or bimetallic substrate binding via formal *two-electron* oxidations of the metal(s) involved. The present report describes the first example of a *one-electron oxidative addition* to a bimetallic complex. The process described herein is particularly novel since it is also characterized by both bimetallic substrate binding and an unprecedented ligand rearrangement.

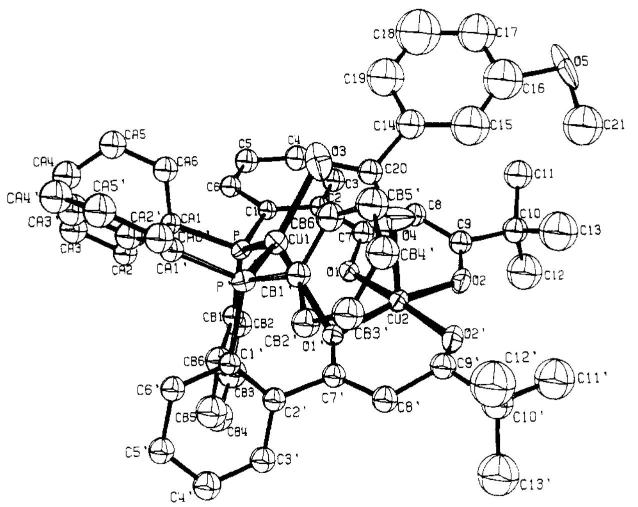

Figure 1. ORTEP plot of the nonhydrogen atoms of the $Cu_2(acacP)_2(3\text{-}CH_3OC_6H_4CO_2)$ molecule with thermal ellipsoids set at the 30% probability level.

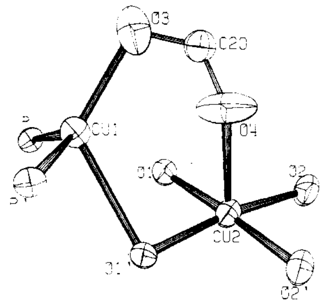

Figure 2. ORTEP plot of the two copper centers with their coordination spheres, including the carboxylate, of the $Cu_2(acacP)_2(3\text{-}CH_3OC_6H_4CO_2)$ molecule with thermal ellipsoids set at the 30% probability level.

Table I. Selected Distances (Å) and Angles (Deg)

Cu1–Cu2	3.321 (2)	Cu2–O2	1.915 (7)
Cu1–P1	2.250 (3)	Cu2–O1′	1.926 (7)
Cu1–P2	2.224 (3)	Cu2–O2′	1.941 (8)
Cu1–O1′	2.524 (7)	Cu2–O4	2.249 (9)
Cu1–O3	2.11 (1)	C20–O3	1.21 (2)
Cu2–O1	1.965 (7)	C20–O4	1.23 (2)
P–Cu1–P′	129.9 (1)	O1–Cu2–O2	91.4 (3)
P–Cu1–O1′	97.4 (2)	O1–Cu2–O1′	88.3 (3)
P–Cu1–O3	104.7 (3)	O1–Cu2–O2′	173.3 (3)
P′–Cu1–O1′	81.4 (2)	O1–Cu2–O4	92.2 (3)
P′–Cu1–O3	119.3 (3)	O2–Cu2–O1′	169.2 (3)
O1′–Cu1–O3	119.8 (3)	O2–Cu2–O2′	86.4 (3)
Cu1–O1′–Cu2	95.6 (3)	O2–Cu2–O4	98.6 (4)
Cu1–O3–C20	107.1 (9)	O1–Cu2–O2′	92.7 (3)
Cu2–O4–C20	133.2 (9)	O1′–Cu2–O4	92.3 (3)
O3–C20–O4	125 (1)	O2′–Cu2–O4	94.3 (4)

Treatment of yellow dichloromethane solutions of the binuclear copper(I) complex of [*o*-(diphenylphosphino)benzoyl]pinacolonate, [Cu(acacP)]$_2$ (**1**), with 1 equiv *or more* of dibenzoyl peroxide results in a rapid color change to green. The lustrous, kelly green crystalline product was obtained in 86% yield by the addition of methanol. While **1** is quite air sensitive in solution, the new complex can be dissolved in polar organic solvents to give aerobically and chromatographically stable solutions. Microanalytical data, osmometry, and

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(4) All new compounds described herein were analyzed satisfactorily for C, H, Cu, and P (e.g., ref 5).

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