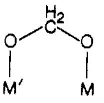
to 1332 and 1225 cm^{-1} in the ^{13}C analogue. These values support the conclusion of considerable single-bond character in the C/O bonds.

$(COD)_2Rh_2OsP_3H_2CO_2$ is the unique example of a neutral compound containing hydride as well as CO_2 ligands. We are, therefore, working to establish conditions that promote the formation of C–H bonds (e.g., formate or the *gem*-diolate I) or indeed the net scission of C/O bonds.



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Acknowledgment. Professor Michele Aresta contributed a remarkably stimulating environment for our contemplation of the results reported here. We thank the National Science Foundation (CHE 83-05281) for financial support and Johnson Matthey, Inc., for material support. Teresa Wright-Kester and Scott Horn are thanked for skilled technical assistance. Drs. A. G. Orpen and D. Ho and Professor A. Albinati provided valuable help with the molecular mechanics calculations.

Supplementary Material Available: Table of atomic positional and thermal parameters for $(COD)_2Rh_2OsH_2CO_2(PMe_2Ph)_3$ (1 page). Ordering information is given on any current masthead page.

Synthesis and Structure of the First Molybdenum-Pterin Complex

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Pterin derivatives have been found in an increasing number of enzymes.[1-3] In a significant number of cases, a metal–pterin complex is present. For example, Mo-co, the molybdenum cofactor contained in at least 10 distinct enzymes, has a 6-substituted sulfur-containing pterin associated with Mo.[2] In phenylalanine hydroxylase, biopterin (a 6-substituted tetrahydropterin) is directly associated with Fe.[3] Despite the presence of metal pterin units in these enzymes, there is no extant report and no structural information yet available about any isolated metal pterin complex. Although several reports are available concerning metal coordination by the related molecules, lumazine and flavin,[4] this paper reports the first characterization and structure determination for a metal–pterin complex.

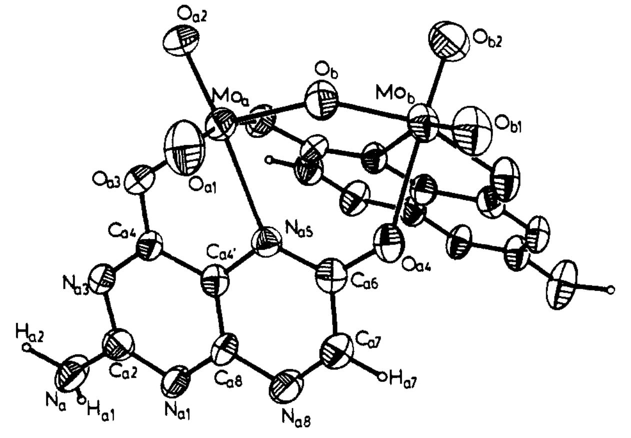

Figure 1. View of $Mo_2O_5(O_2N_5C_6H_3)_2^{2-}$ showing atomic labeling scheme. The atomic numbering scheme of both xanthopterinate ligands is identical. The second xanthopterinate ligand (unlabeled for pictorial clarity) has subscript b in the atomic labels. Thermal ellipsoids drawn at 50% probability. Atom H_{b1} is hidden from view.

Table I. Selected Bond Lengths and Angles Involving the $[Mo_2O_5(O_2N_5C_6H_3)_2]^{2-}$ Anion in Crystalline $[Na((CH_3)_2SO)_2]_2[Mo_2O_5(O_2N_5C_6H_3)_2]$

	Bond Lengths, Å		
Mo_a–O_b	1.883 (6)	Mo_b–O_b	1.884 (6)
Mo_a–O_{a1}	1.691 (7)	Mo_b–O_{b1}	1.710 (6)
Mo_a–O_{a2}	1.707 (5)	Mo_b–O_{b2}	1.684 (7)
Mo_a–O_{a3}	2.084 (5)	Mo_b–O_{b3}	2.081 (5)
Mo_a–N_{a5}	2.324 (6)	Mo_b–N_{b5}	2.324 (6)
Mo_a–O_{b4}	2.252 (6)	Mo_b–O_{a4}	2.246 (6)
$Mo_a\cdot\cdot Mo_b$	3.604 (1)		
	Bond Angles, deg		
$O_bMo_aO_{a1}$	99.6 (3)	$O_bMo_bO_{b1}$	104.9 (3)
$O_bMo_aO_{a2}$	104.2 (3)	$O_bMo_bO_{b2}$	99.4 (3)
$O_bMo_aO_{a3}$	155.5 (2)	$O_bMo_bO_{b3}$	155.3 (2)
$O_bMo_aN_{a5}$	84.7 (2)	$O_bMo_bN_{b5}$	84.3 (2)
$O_bMo_aO_{b4}$	84.9 (2)	$O_bMo_bO_{a4}$	84.8 (2)
$O_{a1}Mo_aO_{a2}$	105.1 (3)	$O_{b1}Mo_bO_{b2}$	105.3 (3)
$O_{a1}Mo_aO_{a3}$	93.5 (3)	$O_{b1}Mo_bO_{b3}$	91.4 (2)
$O_{a1}Mo_aN_{a5}$	92.2 (3)	$O_{b1}Mo_bN_{b5}$	158.3 (3)
$O_{a1}Mo_aO_{b4}$	167.5 (3)	$O_{b1}Mo_bO_{a4}$	84.6 (3)
$O_{a2}Mo_aO_{a3}$	92.1 (2)	$O_{b2}Mo_bO_{b3}$	93.8 (3)
$O_{a2}Mo_aN_{a5}$	158.6 (3)	$O_{b2}Mo_bN_{b5}$	92.3 (3)
$O_{a2}Mo_aO_{b4}$	84.9 (3)	$O_{b2}Mo_bO_{a4}$	167.6 (3)
$O_{a3}Mo_aN_{a5}$	74.1 (2)	$O_{b3}Mo_bN_{b5}$	74.4 (2)
$O_{a3}Mo_aO_{b4}$	78.4 (2)	$O_{b3}Mo_bO_{a4}$	78.3 (2)

Xanthopterin, 2-amino-4,6-dioxopteridine, is a yellow pigment first isolated from butterfly wings ("xanthos" and "pterin" are Greek for yellow and wing, respectively).[5] Under appropriate conditions,[6] xanthopterin reacts with molybdate to form the di-

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[6] (a) Xanthopterin hydrate (Aldrich) (0.397 g, 2.00 mmol), $Na_2MoO_4\cdot 2H_2O$ (0.242 g, 1.00 mmol), and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.176 g, 0.143 mmol) were charged into a 100-mL Schlenk flask. Dimethyl sulfoxide, Me_2SO (50 mL), was added and the mixture was deaerated by multiple purges with argon on the vacuum manifold. Complete dissolution occurred when the mixture was heated to 80 °C. After stirring for 50 min between 85 and 90 °C, the yellow-orange solution was cooled. All Me_2SO was removed by distillation in vacuo. The resulting oil was redissolved in dry, deaerated dmf (20 mL) and the product was precipitated by addition of anhydrous deaerated diethyl ether. The yellow-orange microcrystalline solid was isolated by filtration to give 94% yield of $[Na(dmf)_2]_2Mo_2O_5(xanth)_2$. Satisfactory analysis was obtained for $C_{24}H_{34}N_{14}O_{13}Na_2Mo_2$ (C, H, N, Na, Mo). ^{1}H NMR (Me_2SO-d_6, in ppm downfield from TMS): δ 2.71, 2.87 (s, 12 H, CH_3 of DMF); 6.19 (s br, 2 H, -NH_2 of xanthopterinate); 7.84 (s, 1 H, H7 of xanthopterinate); 7.93 (s, 2 H, dmf). ^{13}C NMR (Me_2SO-d_6, in ppm from TMS): δ 30.8, 35.8, 162.5 (s, dmf resonances); 116.7, 149.2, 160.2, 161, 150.6, 172.5 (s, xanthopterinate resonances). $[Na(dmf)_2]_2Mo_2O_5(xanth)_2$ has one irreversible reduction at −1.295 V vs. Ag/AgCl in 0.1 M $[TBA][PF_6]$DMF. (b) $[TEA]_2Mo_2O_5(xanth)_2$ can be prepared by following the above procedure but substituting TEA_2MoO_4 for $Na_2MoO_4\cdot 2H_2O$. ^{1}H NMR (Me_2SO-d_6): δ 1.18, (t, 12 H, CH_3 of TEA); 3.22 (q, 18 H, CH_2 of TEA), 6.10 (s, 2 H NH_2 of xanthopterinate); 7.77 (s, 1 H, N7 of xanthopterinate).

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anionic chelating and bridging ligand xanthopterinate (=xanth).

$$(A)_2MoO_4\cdot 2H_2O + {}^1/_7(NH_4)_6Mo_7O_{24}\cdot 4H_2O + \\ A = Na, TEA \\ 2\ \text{xanthopterin} \xrightarrow[80\ °C,\ <1\ h]{Me_2SO} (A)_2Mo_2O_5(\text{xanth})_2$$

Use of ammonium heptamolybdate in the reaction is critical to formation of the product in high yields. The dinuclear complex is moisture sensitive and degrades in the atmosphere or in wet solvents to xanthopterin and an unidentified polymolybdate. The dimeric complex does not react with triphenyl phosphine when heated at 110 °C for 4 h. However, treatment with the protic reactants dithiothreitol (dttH_2) or 3,4-toluenedithiol (tdtH_2) precipitates xanthopterin with formation of a molybdenum-oxo-dtt complex or Mo(tdt)$_3$, respectively, as identified by TLC.

The electronic spectrum of xanthopterin in DMF shows an absorption at 390 nm (ϵ = 3360 cm^{-1} M^{-1}) that shifts to 424 nm (ϵ = 2400 cm^{-1} M^{-1}) upon deprotonation to the dianionic form in strong base.[8] The corresponding λ_{max} for the Na$^+$ and TEA$^+$ salts of $Mo_2O_5(\text{xanth})_2{}^{2-}$ in DMF are 418 nm (ϵ = 6820 cm^{-1} M^{-1}) and 424 nm (ϵ = 6910 cm^{-1} M^{-1}), respectively, suggesting that xanthopterin exists in a doubly deprotonated form in the molybdenum complex. Infrared data[9] from both salts of the dimer suggest coordination through both oxygen atoms of the pterin since the strong $\nu_{C=O}$ absorptions of xanthopterin at 1680 and 1660 cm^{-1} are absent in the product spectrum. Absorptions typical[10] of terminal Mo=O and bridging Mo-O-Mo groups of the [$Mo_2O_5{}^{2+}$] unit were observed near 930, 900 cm^{-1} and 785, 765 cm^{-1}, respectively.

The crystal structure[13] of $[Na(Me_2SO)_2]_2Mo_2O_5(\text{xanth})_2$ confirms the chelation mode of the xanthopterin ligand. One view of the oxo-molybdenum dianion is shown in Figure 1. Selected bond distances and angles are given in Table I.

The dimolybdenum dianion consists of a *syn*-[$Mo_2O_5{}^{2+}$] unit chelated and bridged by two xanthopterinate ligands. A noncrystallographic molecular 2-fold symmetry axis passes through the bridging oxygen in a plane perpendicular to the Mo-Mo axis. In $[Mo_2O_5(\text{xanth})_2]^{2-}$ coordination of the two oxygen atoms of each pterin ligand to different Mo atoms favors formation of the less common *syn*-$[Mo_2O_5]^{2+}$ unit.[11] Each molybdenum is bound to O3 and N5 of one xanthopterin forming a five-membered chelate ring analogous to that of 8-hydroxyquinolinate. This binding mode is analogous to the "primary binding site"[4f] observed in flavins coordinated to Ru(II),[4e] Cu(I), Cu(II),[4f] and Ag(I).[4g] The second oxygen atom, O4, bridges the xanthopterin ligand to the second molybdenum. The inner coordination sphere about each Mo is a distorted octahedron (see Table I) of one nitrogen and five oxygen atoms. The two terminal Mo-oxygen bond lengths on each Mo atom are slightly different, likely due to the interaction of the sodium counterions with O_{a2} and O_{b1}.

The pterin rings are planar and this planarity extends through the Mo bound to atoms O3 and N5. The dihedral angle between pterin planes is 47.3°, a value very close to the angle observed in a related catecholate complex, [Mo_2O_5(3,5-dibutylcatecholate)$_2$].[11a] The sodium cations establish a three-dimensional crystal lattice by connecting the dianions. Each of the counterions is bound to one terminal oxo ligand and one xanthopterin oxygen and connects to adjacent dianions through pterin nitrogens N1 and N8. The remaining coordination sites of each six-coordinate sodium atom are filled by oxygen atoms of two dimethyl sulfoxide solvent molecules.

Coordination of xanthopterin by molybdenum has a large effect on the ligand's fluorescence properties. Chelation quenches the fluorescence intensity by 95% compared to that of free xanthopterin. The close resemblance of the spectra from solutions of the Mo dimers to that of xanthopterin suggests that the observed fluorescence is due to dissociated, neutral ligand (formed by trace acid hydrolysis). Previously, the disappearance of fluorescent character in pterins has been attributed to their reduction of di- and tetrahydro forms.[12] Clearly, metal coordination also leads to fluorescence quenching.

The results of these initial studies on molybdenum-pterin coordination chemistry show (a) structural proof for molybdenum coordination through endocyclic nitrogen atoms and exocyclic oxygen atoms in pterin heterocycles and (b) effective quenching of a highly fluorescent pterin by coordination to molybdenum.

Registry No. $Na_2Mo_2O_5(\text{xanth})_2$, 105139-37-5; $[TEA]_2Mo_2O_5(\text{xanth})_2$, 105226-34-4; Mo(tdt)$_3$, 10507-75-2; dtt, 3483-12-3; Mo, 7439-98-7; $[Na/(Me_2SO)_2]_2Mo_2O_5(\text{xanth})_2$, 105227-46-1; xanthopterin, 119-44-8; MO, 7439-98-7.

Supplementary Material Available: Tables of atomic coordinates and anisotropic thermal parameters for non-hydrogen atoms (6 pages); structure factor tables for $[[Mo(O)_2(O_2N_5C_6H_3)]_2O]\text{-}Na_2\cdot 4(CH_3)_2SO$ (18 pages). Ordering information is given on any current masthead page.

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(7) Pariyadath, N., manuscript in preparation.

(8) TEA$_2$(xanth) was prepared by dissolving xanthopterin in methanol by dropwise addition of 2 equiv of TEAOH (as a 25% methanolic solution) then precipitating the salt with diethyl ether.

(9) Infrared data (KBr, cm^{-1}): $[Na\cdot(dmf)_2]_2Mo_2O_5(\text{xanth})_2$ ν_{NH} 3395 s, 3340 s; $\nu_{C=O}$(dmf) 1663 vs; $\nu_{C-O,C-N}$ 1616 m, 1565 s, 1538 vs; $\nu_{Mo=O}$ 934 s, 906 sh, 902 s; $\nu_{Mo-O-Mo}$ 782 ms, 768 m; ν_{Mo-O},ν_{Mo-N}(ligand) 683 w, 665 m, 630 m, 560 m. $TEA_2Mo_2O_5(\text{xanth})_2$ ν_{NH} 3415 s, 3305 m; $\nu_{C=O,C=N}$ 1620 m, 1554 vs, 1538 s; $\nu_{Mo=O}$ 926 s, 904 s, 899 s, 894 sh; $\nu_{Mo-O-Mo}$ 785 ms, 760 s; ν_{Mo-O},ν_{Mo-N}(ligand) 684 w, 629 m, 616 m, 552 m.

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(13) Crystals of $[Na(Me_2SO)_2]_2[Mo_2O_5(\text{xanth})_2]$ were grown from Me$_2$SO/THF. A yellow-orange rectangular parallelepiped of approximate dimensions 0.45 × 0.45 × 0.52 mm was glued to the inside of a thin-walled capillary and sealed with mother liquor. Data were collected on a Nicolet four-circle autodiffractometer using Mo Kα radiation and the structure was solved by Dr. Cynthia Day of Crystalytics Co. The compound crystallizes in the triclinic lattice system, space group $P1$, having cell dimensions a = 9.404 (2) Å, b = 9.412 (2) Å, c = 23.721 (5) Å and α = 92.18 (2)°, β = 92.01 (2)°, γ = 90.22 (2)° giving V = 2097 (1) Å^3 and a calculated density of 1.560 g/cm^3 for Z = 2. The structure was solved by using direct methods. Hydrogen atoms on amino nitrogens N_a and N_b were located from a difference Fourier synthesis and refined as isotropic spheres. All other hydrogen positions were calculated assuming C-H distances of 0.96. Final least-squares refinement on 551 parameters used 4085 unique data having $I > 3\sigma(I)$ and gave residuals R = 4.8 and R_w = 5.6% and GOF of 2.63.

Phenyl-Capped Octaaniline (COA): An Excellent Model for Polyaniline

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In this paper we report that the title compound can be characterized in three stable oxidation states: the reduced, COA (leuco, B_7),[1] the fully oxidized (tetraquinone imine, "TQI", B_3Q_4, old nomenclature "pernigraniline"), and the intermediate oxidation state, B_5Q_2 ("emeraldine"). The properties of these materials, particularly as a function of pH, showed that B_5Q_2 is an excellent model of polyaniline (PANI) because it exhibits all the properties of the polymer, particularly Brönsted acid doping.[2]

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(1) Besides the two capping phenyl groups, in COA there are seven *p*-phenylene rings (benzenoid group, B) in the backbone. Oxidation of one of the backbone B's produces a quinone imine (quinonoid group, Q); the resulting backbone would then be B_6Q. Thus this nomenclature: B_7 (COA), B_6Q (COA-BI), B_5Q_2 (COA "emeraldine"), B_4Q_3 (COA-"nigraniline"), and B_3Q_4 [COA pernigraniline or tetraquinone imine (TQI)].

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