3 should also be planar. This would lead to the formation of quite strong N–Ru π bonds as depicted in Figure 2. Absence of electrons on the π* level should stabilize this system.

Although we have been unable to perform X-ray structure determinations of 3, the eclipsed orientation of the axial diphenylamido ligands is suggested by the following lines of evidence. (i) The equivalence of the ortho protons and the equivalence of the *m*-methoxy protons or the porphyrin ring phenyl group shown in the ^{1}NMR spectrum of 3 indicate mirror symmetry in the porphyrin plane for the solution structures. This mirror symmetry should be absent for the staggered orientation of the $^-NPh_2$ groups. (ii) An eclipsed orientation of the SPh_2 groups in the $Ru^{II}(OEP)(SPh_2)_2$, which contains only a small degree of Ru–S π back-bonding, has even been observed by James and co-workers through X-ray crystallographic studies.[16a] It seems likely that complexes $Ru(OEP)(SPh_2)_2$ and 3 have similar structures, and the latter should favor this orientation to a larger extent owing to N–Ru–N π bonding. (iii) A staggered orientation of the two $^-NPh_2$ groups would cause 3 to be paramagnetic, which is in contrast with the observed diamagnetism of 3. (iv) The singlet of the pyrrole proton resonances (H_β) of 3 observed in the room-temperature ^{1}H NMR spectrum is not incompatible with the presumed structure of D_{2h} symmetry for 3. Although p_x-(N)–d_{xz}(Ru)–p_x(N) π bonding would lower the symmetry of the porphyrin, leading to the splitting of the pyrrolic protons into two sets (H_a and H_b) as shown in Figure 3, we do not expect that this bonding is so strong as to prevent the rotation of diphenylamide groups. The shuttling of the molecule of 3 between the diamagnetic conformations I and II would be rapid, leading to the observation of a singlet for the pyrrole proton resonances in the ^{1}H NMR measurements even at −45 °C.

In addition, the IR spectrum of 3 shows no N–H stretching bands. The "oxidation state marker" band[20] (sharp and strong) appears at 1012 cm^{-1}, which is consistent with the +4 oxidation state of ruthenium.

3 is air-stable in the solid state. In dichloromethane solution, it exhibits no quick reaction with alcohol and triphenylphosphine. Oxidation of 3 with *m*-CPBA afforded the dioxo complex 2.

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(20) Our studies on metalloporphyrins indicated that this band was very useful to the characterization of both ruthenium and osmium TPP or substituted-TPP complexes. See also: Groves, J. T.; Ahn, K.-H. *Inorg. Chem.* **1987**, *26*, 3831. The "oxidation state marker" bands of 1 and 2 are 1007 and 1019 cm^{-1}, respectively. The bis(amine)ruthenium(II) porphyrins $Ru(Por)(NH_2R)_2$ and $Ru(Por)(NHR_2)_2$ (see text) show the "oxidation state marker" bands ranging from 998 to 1004 cm^{-1}.

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Syntheses and X-ray Structures of Novel Phenoxo-Bridged Binuclear Complexes: Bis(μ-phenoxo)bis[bis(acetylacetonato)chromium(III)] and Its Para-Substituted Phenoxo Analogues

In contrast to a relatively large number of hydroxo- or alkoxo-bridged binuclear complexes,[1-5] there have been only a very limited number of binuclear complexes bridged by single phenoxo ligands[6] but not by phenoxo groups attached as part(s) of multidentate ligands. Such μ-(4-substituted-phenoxo) binuclear complexes of chromium(III) are expected to be one of the most appropriate series which will make possible relating the magnetic interactions to the structural and electronic properties of bridging moieties in comparison with those of similar types of binuclear complexes. We report here a new versatile synthetic route to the novel title binuclear (acetylacetonato)chromium(III) complexes bridged not only by X-phO (X = CH_3 (**1**), H (**2**), Cl (**3**), NO_2 (**4**), OCH_3 (**5**)) but also by X-phS (X = H, CH_3) and RO (R = H, CH_3, C_2H_5) together with their characterization, magnetic behavior, and the X-ray structures for two of them (**1**, **2**). Among these complexes, only the alkoxo complexes of analogous types have already been reported.[3,5]

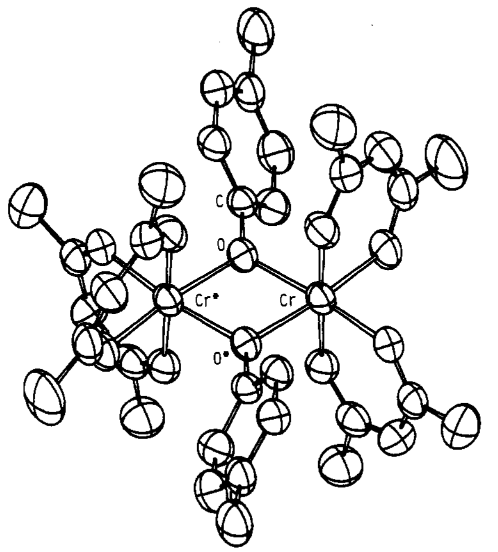

Figure 1. ORTEP drawing of $[Cr_2(acac)_4(CH_3phO)_2]$ (**1**) at the 50% probability level. Hydrogen atoms are not shown for clarity.

Five phenoxo complexes **1–5** of the $[Cr_2(acac)_4(X\text{-}phO)_2]$ type were prepared in good yield by the following method. A mixture of an equimolar amount of *trans*-$[Cr(acac)_2(H_2O)_2]Cl$, 4-X-phenol, and trimethylamine in ethanol was allowed to stand with stirring at room temperature overnight. The color of the solution changed from red to green. The removal of ethanol by a vacuum rotary evaporator gave a green oily residue. From this oily substance, a green complex was extracted with chloroform. After the chloroform was evaporated from this solution, the residue was recrystallized from acetone by refrigeration for a few days. The obtained green crystals were collected, washed with acetone and ether, and dried. The corresponding bis(μ-4-X-thiophenoxo) complexes were prepared by the same method as mentioned above. The bis(μ-hydroxo) and bis(μ-alkoxo) complexes were obtained by the analogous reaction of the starting complex only with trimethylamine in *tert*-butyl alcohol and methanol or ethanol, respectively. It is to be noted that this synthetic method is generally applicable to the binuclear complexes with OR and SR type bridging ligands, which have an extraordinarily wide range of pK_a values from 7 to 16.

In view of the elemental analyses,[7] the solubility in chloroform, and the antiferromagnetism as inferred from the magnetic susceptibility measurements, these complexes are supposed to have a binuclear structure. The X-ray single-crystal analyses for

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(7) Satisfactory elemental analyese for C, H, and/or N or Cr were obtained for all the complexes.

Table I. Structural Data for the Bridging Groups and Magnetic Properties

	1[a]	**2**[a]	μ-MeO[b]
Cr–O, Å[c]	1.992 (2)	1.980 (4)	1.962 (9)[d]
Cr–O*, Å[c]	1.974 (2)	1.977 (5)	
Cr–Cr*, Å[c]	3.087 (1)	3.088 (3)	3.028 (2)
Cr–O–Cr*, deg[c]	102.24 (9)	102.6 (2)	101.0 (3)[d]
θ, deg[e]	4.99	0.134	29.75[d]
φ, deg[e]	64.32	59.63	
2*J*, cm^{-1}[f]	−19.0	−16.9	−9.8

[a] This work. [b] Reference 5. [c] For complexes **1** and **2**, unasterisked atoms are related to asterisked atoms by the C_2 axis. [d] These values are averaged. [e] See text. [f] 2*J* refers to the coupling constant determined from the observed susceptibility data.

complexes **1** and **2**[8] substantiate the binuclear structure, where two octahedral six-coordinated chromium(III) ions are symmetrically bridged by two phenoxo ligands as shown in Figure 1. Both of the complexes are racemic isomers with respect to two configurational chiralities due to three chelating ligands in a chromium(III) ion. Such a racemic form is a rare one found only for a few complexes such as the corresponding μ-methoxo complex,[5] whereas most binuclear Cr(III) complexes of this type generally adopt the meso structure as for the μ-alkoxo 3-halogenoacetylacetonato complexes.[3] The structural data are summarized in Table I. The Cr–O and Cr–Cr distances and the Cr–O–Cr angles of the bridging moiety in both complexes are almost the same, but the former distances and the latter angles are a little longer and larger, respectively, than those of the μ-methoxo homologue. The phenyl planes and the Cr_2O_2 bridging plane are twisted with the angles φ ca. 60°. The dihedral angles between the C–O bond vectors of the phenoxo ligands (θ) for the present complexes are much smaller than those of the μ-methoxo homologue, implying the predominant sp^2 hybridization at the bridging phenoxo oxygen ligators.

The UV–vis absorption spectra show no significant difference between these complexes[9] in spite of the large variation of pK_a values for the bridging ligands. The temperature-dependent magnetic susceptibility measurements for the complexes **1** and **2** reveal antiferromagnetic exchange interactions. As expected from the Glerup–Hodgson–Pedersen (GHP) model,[10] the coupling constants (2*J*) for the phenoxo complexes with smaller θ angles become larger than those for the alkoxo ones as shown in Table I. A change from **2** to **1** with a very small increase in θ angles brings about an increase in the coupling constants, contrary to the expected decrease with an increase in the θ angles in terms of the GHP model.[10] The preliminary results for all the present μ-(4-X-phenoxo) complexes with almost constant geometry in the bridging moieties demonstrate that the magnetic interactions in these phenoxo complexes tend to increase with increasing pK_a values of 4-X-phenols or the electron density at the bridging oxygen ligators. This observation is in accordance with the analogous one for Cu(II) complexes.[11] The present correlation will provide a suitable criterion to evaluate the electronic contribution to the magnetic interaction by varying the para substituents of the bridging 4-X-phenols.

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Supplementary Material Available: For **1** and **2**, complete tables of crystal data, positional and anisotropic thermal parameters, bond distances, and bond angles and ORTEP diagrams (8 pages); listings of observed and calculated structural factors (7 pages). Ordering information is given on any current masthead page.

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(8) The X-ray crystal structure analyses were carried out at the X-ray Diffraction Service of our Department of Chemistry. The intensity data were collected by a Rigaku AFC-5R diffractometer with use of Mo Kα radiation (λ = 0.71069 Å). The program TEXSAN was used for the calculations. Crystallographic data: **1**, $Cr_2C_{34}H_{42}O_{10}$, *C*2/*c*, *a* = 13.214 (2) Å, *b* = 16.438 (3) Å, *c* = 16.869 (2) Å, β = 101.773 (9)°, *V* = 3587.2 (8) $Å^3$, *Z* = 4, *R* = 0.043, R_w = 0.047 for 5428 independent refractions; **2**·acetone, $Cr_2C_{35}H_{44}O_{11}$, *P*2/*c*, *a* = 10.568 (3) Å, *b* = 11.564 (3) Å, *c* = 16.485 (3) Å, β = 105.93 (2)°, *V* = 1937.3 (8) $Å^3$, *Z* = 2, *R* = 0.065, R_w = 0.068 for 5933 independent refractions.

(9) Selected UV–vis data: [$\sigma_{max}/10^3\ cm^{-1}$ (log ($\epsilon/dm^3\ mol^{-1}\ cm^{-1}$))]: **1**, 16.9 (2.08), 25.6 (2.60); **2**, 16.8 (2.08), 25.5 (2.64); **3**, 16.8 (2.09), 25.6 (2.64); **4**, 17.0 (2.16); **5**, 16.9 (2.13), 25.6 (2.66).

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Dissolution of Uranium Metal Using Iodine and 2-Propanol. Synthesis and X-ray Crystal Structure of Tetraiodotetraisopropoxybis(2-propanol)diuranium

Direct oxidation of reactive metals with alcohols has been used to prepare a range of metal alkoxide compounds.[1-4] In some systems, small amounts of mercuric halides are added to assist the oxidation and thus formation of the metal alkoxides. Despite the high reactivity of uranium metal, attempts in our laboratories to cleanly prepare uranium alkoxides by direct reaction of the metal with alcohols have not been entirely successful. Reaction of uranium metal in refluxing ethanol or 2-propanol does initially give small amounts of a green, presumably U(IV) alkoxide; however, the metal surface is eventually passivated, and the reaction stops. In contrast, direct oxidation of actinide metals to the metal halides has been reported using a number of halogen transfer agents.[5-7] Clark and Sattelberger found that reaction of uranium metal with $^3/_2$ equiv of I_2 in coordinating solvents leads to the formation of UI_3L_4 species (L = solvent molecule) of significant synthetic utility.[5] Karraker reported the formation of similar actinide complexes, $AnI_3(THF)_x$ (An = Pu, *x* = 5; An = Np, *x* = 4) by reaction of the metals with $C_2H_4I_2$ in THF solutions.[6] We sought to extend this chemistry to the preparation of uranium alkoxides through simultaneous iodine and alcohol oxidation of uranium metal. This type of oxidation has been reported for cerium metal using 2-methylpropan-2-ol as the solvent.[8] The product of the reaction, a presumed cerium–iodo–alkoxide catalyst for oxidation of alcohols, was never isolated and characterized.

Reaction of cleaned uranium metal turnings[5] with I_2 in 2-propanol under anaerobic conditions results in complete dissolution of the metal in a matter of hours (eq 1). A light purple solution

$$U + \geq 1I_2 + 2HO\text{-}i\text{-}Pr \xrightarrow{HO\text{-}i\text{-}Pr} UI_2(O\text{-}i\text{-}Pr)_2(HO\text{-}i\text{-}Pr)_2 + H_2 \tag{1}$$

results from which lavender crystals of a compound formulated as $UI_2(O\text{-}i\text{-}Pr)_2(HO\text{-}i\text{-}Pr)_2$ (**1**) can be isolated by reducing the volume of the solution and cooling to −35 °C.[9] In this reaction,

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