

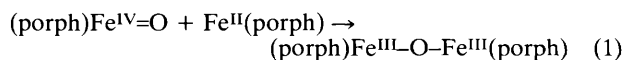
The Synthesis of Heterobinuclear μ -Oxo Complexes containing Cr–O–Mn, Cr–O–Mo, Mo–O–Fe, and Cr–O–Fe Combinations

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Redox reactions between bis(diethyldithiocarbamato)dioxomolybdenum(vi) [(Et₂NCS₂)₂MoO₂] or $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinato-oxochromium(iv) [(TPP)CrO] and Fe^{II}, Mn^{II}, or Mo^{IV} complexes bearing pentadentate salicylideneamine or dithiocarbamate ligands lead to the formation of heterobinuclear μ -oxo bridged complexes; some degree of magnetic coupling is observed between each combination of metals.

One route to the formation of homobinuclear μ -oxo bridged compounds involves a redox reaction between two compounds of the same element in different oxidation states, one of which bears an oxo group which, most likely, forms the bridged intermediate which allows the electron transfer process to occur. The final state in the reaction of oxygen with iron(II) porphyrins leading to μ -oxo iron(III) derivatives is proposed to be of this type¹ [reaction (1)], while the formation of [(Et₂NCS₂)₂Mo^V(O)]₂O by reaction between [Et₂NCS₂]₂-Mo^{VI}O₂ and [Et₂NCS₂]₂Mo^{IV}O has been directly observed.²

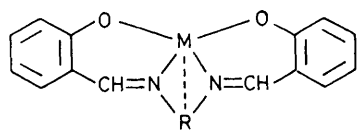


We have reported that the Cr^{IV}=O porphyrin complexes can undergo similar redox reactions with Fe^{II} porphyrins and Fe^{II} phthalocyanine, leading to the formation of Cr–O–Fe hetero-

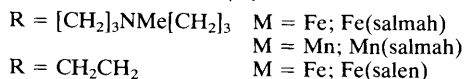
binuclear μ -oxo bridged complexes.^{3,4} It has subsequently been found possible to use such redox reactions to prepare further heterobinuclear oxo-bridged complexes having the metal combination Cr^{III}-O-Mn^{III}, Cr^{III}-O-Mo^V, and Mo^V-O-Fe^{III}. The oxidants used have included the chromium(IV) porphyrin complex (TPP)Cr^{IV}=O (TPP = $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinato) and the Mo^{VI}-oxo-diethyldithiocarbamate compound (Et₂NCS₂)₂Mo^{VI}O₂.

The reductants have included Fe^{II} and Mn^{II} complexes of pentadentate salicylideneamines (1) and dithiocarbamates and the Mo^{IV} species (Et₂NCS₂)₂Mo^{IV}=O. The Fe^{II} and Mn^{II} complexes are known to be oxidised readily with molecular oxygen, the salicylideneamine derivatives forming μ -oxo homobinuclear derivatives;^{5,6} the Mo^{IV}-oxo complex, however, forms (Et₂NCS₂)₂Mo^{VI}O₂.⁷

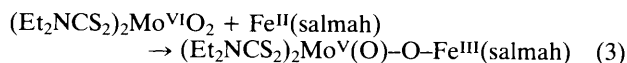
Reactions occur readily in dry tetrahydrofuran solution with careful exclusion of oxygen and the products are precipitated



(1)



by addition of hexane. Typical reactions may be represented as in equations (2) and (3).



Additional $\text{Cr}^{\text{III}}\text{O}-\text{Fe}^{\text{III}}$ complexes have also been prepared using $(\text{TPP})\text{CrO}$ as oxidant and a variety of iron(II) complexes of tetradentate and pentadentate salicylideneamines and bidentate dithiocarbamates.† I.r. spectral bands due to the presence of $\text{Mo}^{\text{V}}=\text{O}$ bands have been identified for $(\text{Et}_2\text{NCS}_2)_2\text{Mo}(\text{O})-\text{O}-\text{Fe}(\text{salmah})$ (933 cm^{-1}) and $(\text{TPP})\text{Cr}-\text{O}-\text{Mo}(\text{O})(\text{Et}_2\text{NCS}_2)_2$ (930 cm^{-1}). The homobinuclear analogue⁸ $[(\text{Et}_2\text{NCS}_2)_2\text{Mo}(\text{O})]_2\text{O}$ is reported to show a corresponding frequency at 932 cm^{-1} . Clearly defined bands relating to the $\text{M}-\text{O}-\text{M}'$ vibrations have not so far been identified for any of the complexes isolated, but a variety of bands can be observed for the Mo^{V} complexes in the $700-800\text{ cm}^{-1}$ region where $\text{Mo}-\text{O}-\text{Mo}$ frequencies have been previously located.⁸

The microanalytical data for a number of the compounds so far isolated indicate the presence of a molecule of H_2O although clear i.r. spectral evidence for its presence has only been observed for several complexes. Similar observations have been reported for the $\text{Cr}-\text{O}-\text{Fe}$ porphyrin derivatives.⁴ Crystallographic evidence has confirmed that in $(\text{TPP})\text{Cr}-\text{O}-\text{Fe}(\text{porph})$ complexes, co-ordination of a donor molecule such

† The complexes are stable in solution in a variety of anhydrous polar solvents under nitrogen but rapidly decompose in the presence of air. Several of the Mo complexes form $(\text{Et}_2\text{NCS}_2)_2\text{Mo}^{\text{VI}}\text{O}_2$ in the presence of air together with oxo complexes of the partner-metal.

Table 1. Magnetic moments of heterobinuclear μ -oxo complexes.

	$\mu_{\text{eff}}/\mu_{\text{B}}$ at 300 K	Calc. spin-only moments/ μ_{B}
$(\text{TPP})\text{Cr}-\text{O}-\text{Mn}(\text{salmah})\cdot\text{H}_2\text{O}$	5.3	(d^3-d^4) 6.2
$(\text{TPP})\text{Cr}-\text{O}-\text{Fe}(\text{salmah})\cdot\text{H}_2\text{O}$	3.2	(d^3-d^5) 7.1
$(\text{TPP})\text{Cr}-\text{O}-\text{Fe}(\text{salen})\cdot\text{H}_2\text{O}$	3.3	(d^3-d^5) 7.1
$(\text{TPP})\text{Cr}-\text{O}-\text{Mo}(\text{O})(\text{Et}_2\text{NCS}_2)_2\cdot\text{H}_2\text{O}$	3.6	(d^3-d^1) 4.3
$(\text{Et}_2\text{NCS}_2)_2\text{Mo}(\text{O})-\text{O}-\text{Fe}(\text{salmah})$	5.3	(d^1-d^5) 6.2

as pyridine occurs at Cr not Fe, suggesting that water may also be co-ordinated to Cr in the present group of compounds.

The magnetic moments of the compounds show an interesting variety of behaviour (Table 1). The $\text{Cr}-\text{O}-\text{Fe}$ complexes display considerably lower moments than those calculated on the basis of a spin-only uncoupled system. The $\text{Cr}-\text{O}-\text{Fe}$ porphyrin derivatives previously studied⁴ show similarly low moments at room temperature and the new compounds are expected to show comparable antiferromagnetic behaviour at lower temperatures. There are similar but less marked reductions in moments for the $\text{Cr}-\text{O}-\text{Mn}$, $\text{Cr}-\text{O}-\text{Mo}$, and $\text{Mo}-\text{O}-\text{Fe}$ complexes. The homobinuclear compound $[(\text{Et}_2\text{NCS}_2)_2\text{Mo}^{\text{V}}(\text{O})]_2\text{O}$ is known to be antiferromagnetically coupled⁹ with a moment of $0.5\mu_{\text{B}}$ at room temperature.

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