by the fact that from 1:1 reaction mixtures complex IV is obtained as the major product. Since the rates of reduction of the two stages differ only by one order of magnitude a standard consecutive reaction treatment was employed to evaluate first-order rate constants.[14] No dependence of rates on $[H^+]$ was detected. The kinetic data are listed in Tables III and IV. Activation parameters for the first stage ($\Delta H^{\ddagger}_1 = 13 \pm 1$ kcal mol^{-1}, $\Delta S^{\ddagger}_1 = -15 \pm 3$ cal K^{-1} mol^{-1}) are consistent with substitution into $[V(H_2O)_6]^{2+}$ controlled inner-sphere mechanism. The values found for the second stage are quite different ($\Delta H^{\ddagger}_2 = 7 \pm 1$ kcal mol^{-1}, $\Delta S^{\ddagger}_2 = -40 \pm 2$ cal K^{-1} mol^{-1}). They are not characteristic for an inner-sphere process. They are remarkably similar to other known outer-sphere reactions of mononuclear Co(III) complexes with V^{2+}.[15]

Discussion

The important structural feature of complex I is the lack of a suitable functional group at the aromatic ring which is available for precursor complex formation with the reductants Cr^{2+} or V^{2+}. The kinetic data of the reductions of the first Co(III) center of complex I can therefore be regarded as typical for outer-sphere mechanisms.[16] This assignment is supported by a rate ratio, k_{Cr}/k_V, of 0.021.

The trinuclear complex II has one uncomplexed carboxylic oxygen adjacent to a $Co(NH_3)_5$ moiety. This Co(III) center is rapidly reduced by Cr^{2+} via an inner-sphere mechanism with attack of the reductant at the uncomplexed carbonyl oxygen; a mixed $Co(III)_2$–Cr(III) complex V is formed. Further reduction of Co(III) proceeds slowly and from the rate ratio it is concluded that an outer-sphere mechanism is operative. It is noted that the second-order rate constants for the reductions of the first Co(III) of complex II and of the mononuclear terephthalatopentaamminecobalt(III) are identical within experimental error.[5]

V^{2+} reacts with complex II in a fast–slow sequence, too. The first stage corresponds to the inner-sphere reduction of the $Co(NH_3)_5$ moiety, and due to the kinetic lability of V(III) complexes the binuclear complex IV can be isolated. This species is subsequently reduced by V^{2+} via an outer-sphere mechanism.

Complexes III and IV are slowly reduced by Cr^{2+} at rates comparable with the one observed for complex I. Although these complexes contain a bridging ligand with good conjugation and a suitable "lead in" functional group, an inner-sphere mechanism with attack of the reductant at the remote carbonyl oxygen appears not to be an energetically favorable path. From the rate ratio outer-sphere mechanisms can be assigned for the reductions of both complexes by Cr^{2+} and V^{2+}.

These results clearly demonstrate that terephthalic acid does not mediate electrons efficiently from one carboxylic group through the benzene ring to the remote Co(III) (inner-sphere: remote attack); whereas it is possible to transfer an electron across a carboxylic group if one Co(III) is coordinated to one oxygen of the carboxylic group (inner-sphere: adjacent attack).

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Registry No. I, 59753-09-2; II, 59780-56-2; III, 58482-23-8; IV, 59753-11-6; Cr^{2+}, 22541-79-3; V^{2+}, 15121-26-3; V, 59753-12-7; tri-μ-hydroxo-bis[triamminecobalt(III)] perchlorate, 22445-08-5; terephthalatopentaamminecobalt(III) perchlorate, 59753-14-9.

Supplementary Material Available: Table II showing kinetic data for the reductions of complexes I–IV by chromium(II) and Table III showing kinetic data for the reductions by vanadium(II) (2 pages). Ordering information is given on any current masthead page.

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The Defect Model and Oxidation State of Europium and Molybdenum in Eu_xMoO_4

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A new series of tetragonal scheelite-type compounds with stoichiometry Eu_xMoO_4 ($0.67 \le x \le 1.00$) was recently reported by Banks[2] and the scheelite solid-solution series $EuMO_4$–$Eu_2(MO_4)_3$ (M = Mo, W) have also been studied by McCarthy.[3] Unit cell parameters and density measurements suggest a cation vacancy model leading to the formulation $Eu^{II}{}_{1-3y}Eu^{III}{}_{2y}\square MoO_4$ where $y = 1 - x$ and x is the stoichiometric amount of europium in Eu_xMoO_4 (i.e., $Eu^{II}{}_{3x-2}Eu^{III}{}_{2-2x}\square_{1-x}MoO_4$). There is some uncertainty though, concerning the oxidation state of molybdenum, and the possible presence of Mo^V has been postulated.[2] We sought to remove this uncertainty by determining the area ratios of Eu^{II} and Eu^{III} Mössbauer resonance peaks as previously described by Greenwood et al.[4] for the related phases Eu_xWO_4. Our results allow us to rule out the presence of $[Mo^VO_4]^{3-}$ tetrahedra in the series Eu_xMoO_4, though when gadolinium is also present, as in the two-phase mixture of overall composition "$Gd_{0.5}Eu_{0.5}MoO_4$", then the observed Eu^{II}/Eu^{III} ratio can only be explained by the simultaneous partial reduction of molybdenum(VI) or the much less likely reduction of gadolinium(III).

Experimental Section

Samples were prepared as previously described.[2] The material listed as "$Gd_{0.5}Eu_{0.5}MoO_4$" was, in fact, an equimolar mixture of $Gd_{0.85}Eu_{0.15}MoO_4$ and $Gd_{0.15}Eu_{0.85}MoO_4$.

Mössbauer spectra were obtained using Elscint equipment as previously described,[5] with both source and absorber at 4.2 K. The source was 300 mCi $^{151}SmF_3$ and the resonance line widths were in the range 2.4–3.5 mm s^{-1} for Eu^{III} and 4.3–5.7 mm s^{-1} for Eu^{II}. Samples were mounted with a thickness of 10–20 mg of $^{151}Eu/cm^2$ except for "$Gd_{0.5}Eu_{0.5}MoO_4$" which had 6.7 mg of $^{151}Eu/cm^2$. Acceptable spectra were obtained with about 3×10^6 counts per channel.

Results and Discussion

Typical spectra are shown in Figure 1. The most obvious features are the complete lack of any magnetic hyperfine interaction at 4.2 K and the presence of substantial amounts of Eu^{II}. The relative proportions of Eu^{II} and Eu^{III} in the various samples are shown in the Table I. Experimental values were calculated from the areas of the computer-fitted reso-

Table I. Mössbauer Data and Proportions of Eu^{II} and Eu^{III} in Eu_xMoO_4

Material	$\delta(Eu^{II})$,[a] mm s^{-1}	Percentage Eu^{II}		$\delta(Eu^{III})$,[a] mm s^{-1}	Percentage Eu^{III}	
		Exptl	Theor		Exptl	Theor
$Eu_{0.9}MoO_4$	−11.7	73 ± 2	77.8	+0.6	27 ± 1	22.2
$Eu_{0.7}MoO_4$	−12.1	15 ± 2	14.3	+0.6	85 ± 2	85.7
$Eu_{0.67}MoO_4$		0 ± 0.1	0	+0.7	100 ± 0.1	100
"$Gd_{0.5}Eu_{0.5}MoO_4$"	−12.0	55 ± 0.8	See text	+0.9	45 ± 00.7	See text

[a] Chemical isomer shifts δ are quoted relative to EuF_3 as zero.

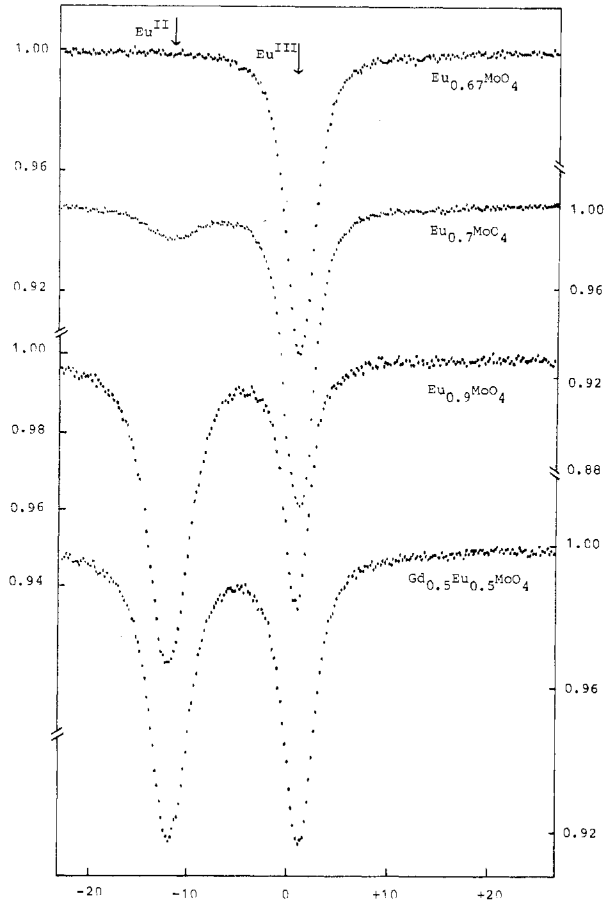

Figure 1.

nances on the assumption that both species have the same Mössbauer recoil-free fraction. The theoretical values were calculated according to the cation vacancy defect model with no contribution from Mo^V. Since saturation effects will tend to decrease the intensity of stronger peaks,[6] the concentration of Eu^{II} in $Eu_{0.9}MoO_4$ will be slightly greater than the uncorrected experimental value of 73% and the concentration of Eu^{III} in $Eu_{0.7}MoO_4$ will be slightly greater than 85%. The close agreement of these values with those calculated on the basis of the cation vacancy model rules out the possibility of any significant reduction of molybdenum to Mo^V and the presence of $[Mo^VO_4]^{3-}$ ions in these phases since this would substantially reduce the concentration of Eu^{II} required for charge balance.

In the case of "$Gd_{0.5}Eu_{0.5}MoO_4$", the two-phase mixture of limiting solid solutions was studied because no samples of the single-phase materials remained from previous work. Table I shows that 45% of all the europium is Eu^{III}. The phase $Gd_{0.85}Eu_{0.15}MoO_4$ contained predominantly $[Mo^VO_4]^{3-}$ ions, implying that both gadolinium and europium are in the 3+ state; this accounts for one-third of the Eu^{III} resonance area. The second phase ($Gd_{0.15}Cu_{0.85}MoO_4$) contains the other two-thirds of the Eu^{III} (i.e., $Eu^{III}_{0.30}$); charge balance then requires that part of the molybdenum in this phase is also present as Mo^V, the detailed formulation being $Gd^{III}_{0.15}Eu^{II}_{0.55}Eu^{III}_{0.30}Mo^V_{0.45}Mo^{VI}_{0.55}O_4$.

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Evidence for a Dissociative Mechanism in the Reaction of Glycine with $Cr(NH_3)_5H_2O^{3+}$. Ionic Strength Contributions (as a 1:1 Electrolyte) and Ion-Pairing(K_{IP}) Ability of the Glycine Zwitterion

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There is at present no general agreement as to the mechanism of substitution of H_2O in aquopentaamminechromium(III), $Cr(NH_3)_5H_2O^{3+}$,[1-4] and the reaction with glycine is of interest in further evaluating the substitution behavior of this complex. Features of the recently studied reaction of oxalate with $Cr(NH_3)_5H_2O^{3+}$ are the initial replacement of H_2O[5] at a rate comparable to that of water exchange,[2] followed by the chelation of the oxalate with displacement of ammonia.[6]

Experimental Section

Materials. The complex $[Cr(NH_3)_5H_2O](ClO_4)_3$ was prepared as previously described.[6,7] Glycine (BDH Analar) was used without further purification. Triply distilled and CO_2-free water was used in making up solutions. Lithium perchlorate was prepared from $HClO_4$ (Analar 72%) and Li_2CO_3 (reagent grade) and recrystallized.

Kinetics. Preliminary experiments on the reaction of $Cr(NH_3)_5H_2O^{3+}$ (5.8×10^{-3} M) with glycine (5.8×10^{-2} M), $[H^+] = (3.2–16) \times 10^{-4}$ M, $I = 1.00$ M, 50 °C, indicated nonretention of isosbestic points and therefore the formation of more than one product. Ion-exchange separation of reactant solutions (for details see ref 6), over periods in which there was up to 50% consumption of $Cr(NH_3)_5H_2O^{3+}$, indicated two products, $Cr(NH_3)_5(O_2CCH_2NH_3)^{3+}$ and $Cr(NH_3)_4(H_2O)(O_2CCH_2NH_3)^{3+}$, which have previously been characterized.[6] The kinetics were monitored at the 506-nm isosbestic point for the two products (ε 39.8 M^{-1} cm^{-1}). Concentration ranges