Table I

atom	x	y	z	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	0.0 (0)	0.05424 (3)	0.25 (0)	2.640 (6)	1.992 (8)	2.349 (6)	0 (0)	1.169 (4)	0 (0)
S1	0.04847 (4)	0.13099 (7)	0.45127 (4)	4.28 (1)	3.24 (2)	2.85 (1)	−1.40 (2)	2.263 (9)	−0.28 (1)
S2	0.11876 (3)	0.28756 (7)	0.33052 (4)	3.56 (1)	3.14 (2)	2.78 (1)	−0.83 (1)	2.138 (8)	−0.31 (1)
O1	0.0810 (1)	−0.0644 (2)	0.2564 (1)	3.85 (5)	3.10 (6)	3.75 (5)	1.13 (5)	1.83 (3)	0.32 (5)
N1	0.1440 (1)	0.3968 (2)	0.5309 (1)	2.91 (4)	2.74 (6)	2.74 (4)	−0.50 (5)	1.77 (3)	−0.29 (5)
C1	0.1099 (1)	0.2879 (2)	0.4490 (1)	2.45 (5)	2.67 (7)	2.37 (5)	−0.22 (5)	1.34 (3)	0.11 (5)
C2	0.1911 (1)	0.5321 (3)	0.5225 (2)	2.70 (5)	2.65 (8)	3.29 (6)	−0.52 (6)	1.61 (4)	−0.24 (6)
C3	0.1343 (1)	0.3951 (3)	0.6323 (2)	4.08 (6)	4.2 (1)	3.31 (5)	−0.83 (7)	2.69 (3)	−0.89 (6)
C4	0.1237 (2)	0.6629 (3)	0.4554 (2)	3.99 (8)	3.2 (1)	5.12 (9)	0.28 (8)	2.07 (6)	0.77 (8)
C5	0.2241 (2)	0.3554 (4)	0.7489 (2)	6.20 (9)	5.4 (1)	3.33 (6)	0.6 (1)	3.07 (5)	0.71 (8)

[a] The form of the anisotropic temperature factor is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

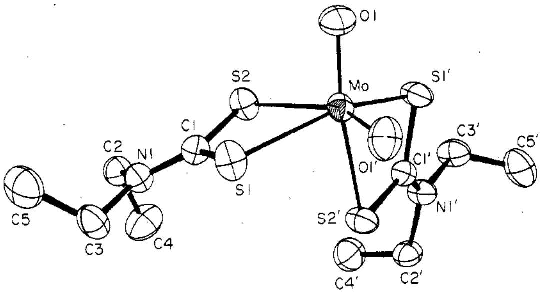

Figure 1. View of $MoO_2(S_2CN(C_2H_5)_2)_2$. The atom labels used in the text are shown.

rection was applied to the complete data set. The systematic absences (hkl, $h + k \neq 2h$; $h0l$, $l \neq 2n$) are consistent with the space groups $C2/c$ and Cc. The structure had been originally solved[7] in the centric space group $C2/c$, and our refinement confirms this choice. The starting coordinates were taken from Kopwillem,[7] transformed so that all of the atoms belong to the same molecule. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms, calculated on the basis of tetrahedral geometries and C–H distances of 0.98 Å, were included as fixed contributions in the final refinement cycles. The orientations of the methyl groups were determined from a difference Fourier map, and the temperature factors for all hydrogen atoms were set equal to 5.0 Å². The structure was refined to $R = 0.030$ and $R_w = 0.038$ with the error in an observation of unit weight equal to 1.12 electrons. Final atomic positional and thermal parameters are compiled in Table I. A listing of observed and calculated structure factors (Table III) is included as supplementary material.

Results and Discussion

The $MoO_2(S_2CN(C_2H_5)_2)_2$ complex has crystallographically imposed twofold symmetry. The overall structure and the atom numbering scheme are shown in Figure 1. The structure is a distorted octahedron with the oxo groups cis to each other and trans to sulfur atoms. The remaining two sulfur atoms are approximately trans to each other. Relevant bond distances and angles are given in Table II.

As expected, these data are substantially different from those found in the original determination[7] and quite similar to those for $MoO_2(S_2CN(C_3H_7)_2)_2$.[8] In particular, the average Mo=O distance and the O=Mo=O angle are 1.703 (2) Å and 105.81 (12)°, respectively, compared to 1.696 (5) Å and 105.7 (1)° for the propyl analogue. The sulfur atoms trans to the oxo groups must compete with the strongly bound oxo groups for the same orbitals.[5] This trans effect is reflected in the Mo–S2 distance of 2.639 (1) Å compared to 2.450 (1) Å for the sulfur atoms trans to each other. The ligand has the expected geometry. The atoms S1, S2, C1, N1, C2, and C3 are essentially coplanar with the greatest deviation from the weighted least-squares plane being 0.04 Å. The Mo atom lies 0.43 Å out of this plaine.

Therefore, the structure of $MoO_2(S_2CN(C_2H_5)_2)_2$ is completely consistent with other dioxomolybdenum structures with similar donor atoms. This constancy of structure for octahedral dioxomolybdenum complexes should be useful in elucidating the structure and the mechanism of action of the metal sites in molybdenum-containing enzymes.

Table II. Selected Bond Angles (Deg) and Distances (Å)

Bond Distances			
Mo–S1	2.450 (1)	C1–N1	1.315 (3)
Mo–S2	2.639 (1)	N1–C2	1.470 (3)
Mo–O1	1.703 (2)	N1–C3	1.478 (3)
S1–C1	1.738 (2)	C2–C4	1.507 (3)
S2–C1	1.700 (2)	C3–C5	1.499 (4)
Bond Angles			
S1–Mo–S1′	148.51 (3)	S2–Mo–S2′	80.06 (3)
S1–Mo–S2	68.76 (2)	S2–Mo–O1	90.75 (6)
S1–Mo–S2′	86.95 (2)	S2–Mo–O1′	155.58 (6)
S1–Mo–O1	110.88 (6)	O1–Mo–O1′	105.81 (12)
S1–Mo–O1′	88.33 (6)		

Acknowledgment. This work was supported by the National Science Foundation through Grant PCM 79-04915.

Registry No. $MoO_2(S_2CN(C_2H_5)_2)_2$, 18078-69-8.

Supplementary Material Available: Table III, a listing of observed and calculated structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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Oxidation of Cerium(III) Phosphate by Steam in the Presence of Lithium Halides and Its Use in Thermochemical Water-Splitting Cycles

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Thermochemical cycles for water splitting[1] employ thermal energy to drive a cyclic series of chemical reactions, the sum of which is just H_2O + thermal energy = $H_2 + {}^1/_2O_2$. Our previous work[2,3] showed that cerium(IV) oxide, CeO_2, reacts with alkali metal hydrogen phosphates—MH_2PO_4 or M_2HPO_4, where M = Li, Na, K—at >600 °C to produce $O_2(g)$, cerium(III) phosphate, $CePO_4$, and alkali metal orthophosphates, M_3PO_4. When M = Na or K, the double phosphate $M_3Ce(PO_4)_2$ forms from the $CePO_4$ and the

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(1) C. E. Bamberger, J. Braunstein, and D. M. Richardson, *J. Chem. Educ.*, **55**, 561 (1978).

(2) C. E. Bamberger, P. R. Robinson, and R. L. Sherman, *Inorg. Chim. Acta*, **34**, L203 (1979).

(3) C. E. Bamberger and P. R. Robinson, *Inorg. Chim. Acta*, in press.

(4) D. R. Stull and H. Prophet, *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)*, **NSRDS-NBS 37** (1971).

0020-1669/80/1319-2181$01.00/0

Table I. Data for Typical Reactions of $CePO_4$ with H_2O^a and LiCl, LiBr, and LiI

mmol of $CePO_4$	LiX, mmol	T_R,[b] °C	T_m,[c] °C	time, h	H_2 yield, mmol	HX yield, mmol
4.97	LiCl, 16.20	680–960	860 ± 15	2.0	2.58 (104%)	15.28 (102%)
16.04	$LiBr{\cdot}H_2O$, 50.42	615–950	885 ± 30	2.5	6.46 (80.5%)	39.39 (80.0%)
15.45	$LiI{\cdot}3H_2O$, 59.08	430–980	875 ± 30	2.5	6.08 (81.5%)	48.82 (105%)

[a] In all of our experiments, the rate at which steam passed over the other reactants was maintained at 4.0 ± 0.8 mL of condensed $H_2O(l)$/min. [b] T_R = range of temperatures over which the observed partial pressure of evolved H_2 exceeded 0.1% in a 100 cm^3/min stream of Ar(g). [c] T_m = temperature at which the observed partial pressure of H_2 reached its maximum value.

Table II. Free-Energies for the Reaction of LiX with $H_2O(g)$ at 927 °C (1200 K)[a]

reaction	ΔG^{1200}, kJ/mol of Li_2O
$2LiF(l) + H_2O(g) = Li_2O(c) + 2HF(g)$	+191
$2LiCl(l) + H_2O(g) = Li_2O(c) + 2HCl(g)$	+176
$2LiBr(l) + H_2O(g) = Li_2O(c) + 2HBr(g)$	+183
$2LiI(l) + H_2O(g) = Li_2O(c) + 2HI(g)$	+160
$Li_2CO_3(l) = Li_2O(c) + CO_2(g)$	+54

[a] Data taken from ref 4.

M_3PO_4.[2] In seeking ways to use these reactions in thermochemical cycles, we discovered that steam will oxidize $CePO_4$ to CeO_2 in the presence of lithium halides—LiX, where X = Cl, Br, I—according to the reaction described by eq 1, where

$$2CePO_4(c) + 6LiX(c,l) + 4H_2O(g) = 2CeO_2(c) + 2Li_3PO_4(c) + 6HX(g) + H_2(g) \quad (1)$$

(c), (l), and (g) refer respectively to the states crystalline, liquid, and gaseous. This paper describes our studies of this reaction and its use in thermochemical cycles based on the Ce(IV)/Ce(III) redox couple.

Results and Discussion

A. Oxidation of $CePO_4$. Table I describes the conditions under which eq 1 proceeds. All of our reactions between LiI, H_2O, and $CePO_4$ showed relatively large differences between the H_2 percent yield and the HI percent yield. These discrepancies can be attributed in part to the steam volatilization of LiI(l) followed by the reaction of LiI with steam and the silica reaction tubes (eq 2). Under our reaction conditions,

$$2LiI(l) + H_2O(g) + SiO_2(c) = Li_2SiO_3(c) + 2HI(g) \quad (2)$$

i.e., in the presence of a steady stream of Ar(g) and $H_2O(g)$, the possibility of this reaction is shown by its ΔG, which is +20.5 kJ at 927 °C; therefore, its $K_{eq} = [HI]^2/[H_2O] = 0.128$. Analysis by X-ray powder diffraction[5] confirmed this explanation. It showed that the white powder which deposited on the inside of the quartz tubes during this reaction was a mixture of LiI and lithium silicates.

Table I also shows that the partial pressure of H_2 evolved in reaction 1 reaches a maximum at about the same temperature for all three lithium halides. This result is reasonable if eq 1 is considered to be the sum of the hypothetical reactions described by eq 3–5. The free energies for reaction 4 (ΔG_4

$$6LiX + 3H_2O = 3Li_2O + 6HX \quad \Delta G_3 \quad (3)$$

$$3Li_2O + 2CePO_4 = Ce_2O_3 + 2Li_3PO_4 \quad \Delta G_4 \quad (4)$$

$$Ce_2O_3 + H_2O = 2CeO_2 + H_2 \quad \Delta G_5 \quad (5)$$

is unavailable) and reaction 5 ($\Delta G^{1200} = -46.5$ kJ[4,6]) will be the same, regardless of X. Only ΔG_3 depends upon the nature of X. As Table II shows, for X = Cl, Br, and I, ΔG_3 varies by only 23 kJ/mol of Li_2O, or 13%, at 927 °C. Because ΔG_3 is always ≥160 kJ for the lithium halides in Table II, $\Delta G_4 + \Delta G_5$ must be less than about −160 kJ at 927 °C. We confirmed this by reacting $CePO_4$ with excess LiOH (eq 6). We obtained 86–100% of the expected H_2 at 400–615 °C—temperatures much lower than those required for reaction 1.

$$2CePO_4 + 6LiOH = 2CeO_2 + 2Li_3PO_4 + 2H_2O + H_2 \quad (6)$$

Table II implies that Li_2CO_3 should participate readily in a reaction similar to that described by eq 1. Our experiments confirmed this implication: The reaction of $CePO_4$ with Li_2CO_3 and H_2O yields CeO_2, CO_2, Li_3PO_4, and H_2 in amounts consistent with eq 7 at 650–800 °C. Details of this particular reaction are reported elsewhere.[3]

$$2CePO_4 + 3Li_2CO_3 + H_2O = 2CeO_2 + 2Li_3PO_4 + 3CO_2 + H_2 \quad (7)$$

B. Reduction of CeO_2. Treatment of CeO_2 with excess LiH_2PO_4 or $Li_3P_3O_9$ (lithium metaphosphate) yields $CePO_4$, Li_3PO_4, and O_2 at temperatures between 480 and 820 °C. The maximum observed partial pressure of O_2 occurred at 670 ± 30 °C. The yields of O_2 ranged from 91 to 102% of that expected, on the basis of the stoichiometry of eq 8 and 9. The

$$3LiH_2PO_4 = Li_3P_3O_9 + 3H_2O \quad (8)$$

$$2CeO_2 + Li_3P_3O_9 = 2CePO_4 + Li_3PO_4 + {}^1/_2O_2 \quad (9)$$

condensation reaction described by eq 8 takes place at temperatures ≥200 °C. CeO_2 can also be reduced to $CePO_4$ by $H_4P_2O_7$ at 550–900 °C, with the maximum partial pressure of O_2 occurring at 600 °C. We detected O_2 in amounts ranging from 60 to 85% of those predicted by eq 10, and analysis by X-ray powder diffraction showed that $CePO_4$ was a product of the reaction. Pyrophosphoric acid and other condensed phosphoric acids such as HPO_3 or P_4O_{10} are formed from H_3PO_4 at temperatures above 220 °C (eq 11).

$$2CeO_2 + H_4P_2O_7 = 2CePO_4 + 2H_2O + {}^1/_2O_2 \quad (10)$$

$$2H_3PO_4 = H_4P_2O_7 + H_2O \quad (11)$$

C. Treatment of Li_3PO_4 with HX. The addition of 3 equiv of HCl, HBr, or HI to Li_3PO_4 converts this rather insoluble phosphate (solubility = 0.03 g/100 g of H_2O at 20 °C[7]) into soluble H_3PO_4 and 3 equiv of the corresponding lithium halide. The partial conversion of Li_3PO_4 to the more soluble LiH_2PO_4 was achieved by treating the orthophosphate with 2 equiv of hydrohalic acid. Li_2HPO_4 does not exist.[8]

D. Ion-Exchange Separation of LiCl or LiBr from H_3PO_4. We tested several methods for separating LiCl or LiBr from H_3PO_4—solvent extraction of the halides into, e.g., amyl alcohol, crystallization of LiCl or LiBr from solutions containing H_3PO_4, and ion-exchange chromatography. (Experiments with LiI were confounded by the facile oxidation of I^- to I_2.) Of these, only ion-exchange chromatography gave satisfactory results. Fractional crystallizations were made difficult by the

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(5) X-ray powder patterns and neutron activation analyses were obtained by the Analytical Division, Oak Ridge National Laboratory.

(6) R. H. Schumm, D. D. Wagman, S. Bailey, W. H. Evans, and V. B. Parker, *NBS Tech. Note (U.S.)*, **No. 270-7** (1973).

(7) A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds", 3rd ed., Van Nostrand, New York, 1940, p 930.

(8) J. C. Bailar, H. J. Emeleus, R. Nyholm, and A. F. Trotman-Dickenson, Eds., "Comprehensive Inorganic Chemistry", Vol. 1, Pergamon, New York, 1973, p 360.

fact that evaporation of $\mathrm{H_2O}$ from solutions containing LiX's and $\mathrm{H_3PO_4}$ gives rise to steam volatilization of $\mathrm{H_3PO_4}$, and some back-reaction of $\mathrm{H_3PO_4}$ with the crystallized LiX's to produce HX and lithium phosphates.

In a typical ion-exchange experiment, 9.9 mmol (29.7 mequiv) of $\mathrm{Li_3PO_4}$ was slurried in water with 8.09 g (20.1 mequiv) of acid-treated Dowex 50W ion-exchange resin. The mixture was filtered, and titration of the resulting solution showed that it contained 1.1 mmol (3.3 mequiv) of $\mathrm{H_3PO_4}$ and 8.2 mmol (16.4 mequiv) of $\mathrm{H_2PO_4^-}$. Therefore, the total dissolved phosphate was 9.3 mmol or 94% of that originally used; 19.7 mequiv of acid was consumed or 98% of that originally used. The $\mathrm{Li^+}$ was then eluted from the resin with excess 1 N HCl; subsequent titration of the acid in the combined eluant solutions showed that 18.8 mequiv of HCl remained on the column, an amount equivalent to 95.4% of the 19.7 mequiv of Li which was adsorbed.

In other experiments, mixtures of $\mathrm{CeO_2}$ and $\mathrm{Li_3PO_4}$ produced from reaction 1 were treated with excess 1 N HCl to dissolve all of the $\mathrm{Li_3PO_4}$. The solution was collected by centrifugation and passed through an acid-treated Dowex 50W column. Titration of the eluant solutions showed that 100.0 ± 0.7% of the $\mathrm{Li_3PO_4}$ had been converted to $\mathrm{H_3PO_4}$. The $\mathrm{Li^+}$ was then eluted from the resin in the manner described above.

The solid products of reaction 1 can be separated prior to treatment with HX by flotation in 1,1,2,2-tetrabromoethylene, but only if the solids are slurried in water first. An $\mathrm{H_2O}$–$\mathrm{Li_3PO_4}$ suspension floats on the $\mathrm{Br_2CHCHBr_2(l)}$; $\mathrm{CeO_2(s)}$ is more dense and sinks to the bottom of the system. In typical experiments, a single treatment yielded a lighter aqueous suspension containing 89% of the $\mathrm{Li_3PO_4}$ and a solid containing all of the $\mathrm{CeO_2}$ and the remainder of the $\mathrm{Li_3PO_4}$.

E. Summary. Combination of These Reactions into Thermochemical Cycles. Reactions 1, 8–11, and those described in section D can be combined into at least two types of thermochemical cycles. Cycle 1 (separation steps are not shown) combines eq 1 with eqs 8 and 9 and the acidification of $\mathrm{Li_3PO_4}$. Note that the sum of all the reactions is just $\mathrm{H_2O = H_2 + {}^1/_2O_2}$. In Cycle 2, eq 1 is combined with eq 10 and 11 and the acidification of $\mathrm{Li_3PO_4}$. The maximum required temperature is the same for both cycles. Cycle 2 is simpler and requires less phosphate, but Cycle 1 avoids the potential problems of dealing with $\mathrm{H_3PO_4}$ at high temperatures. The practicality of both cycles is minimized by need to use an ion-exchange resin for a separation step.

Cycle 1

$$\mathrm{2CePO_4 + 6LiX + 4H_2O = 2CeO_2 + 2Li_3PO_4 + 6HX + H_2} \quad T \simeq 900\ ^\circ\mathrm{C}$$

$$\mathrm{2CeO_2 + Li_3P_3O_9 = 2CePO_4 + Li_3PO_4 + {}^1/_2O_2} \quad T \simeq 700\ ^\circ\mathrm{C}$$

$$\mathrm{3Li_3PO_4 + 6HX = 3LiH_2PO_4 + 6LiX} \quad T = 25\ ^\circ\mathrm{C}$$

$$\mathrm{3LiH_2PO_4 = Li_3P_3O_9 + 3H_2O} \quad T > 200\ ^\circ\mathrm{C}$$

Cycle 2

$$\mathrm{2CePO_4 + 6LiX + 4H_2O = 2CeO_2 + 2Li_3PO_4 + 6HX + H_2} \quad T \simeq 900\ ^\circ\mathrm{C}$$

$$\mathrm{2CeO_2 + H_4P_2O_7 = 2CePO_4 + 2H_2O + {}^1/_2O_2} \quad T \simeq 600\ ^\circ\mathrm{C}$$

$$\mathrm{2Li_3PO_4 + 6HX = 2H_3PO_4 + 6LiX} \quad T = 25\ ^\circ\mathrm{C}$$

$$\mathrm{2H_3PO_4 = H_4P_2O_7 + H_2O} \quad T \simeq 220\ ^\circ\mathrm{C}$$

Experimental Section

A. Reagents. $\mathrm{CeO_2}$ (99.9% pure) was purchased from Gallard-Schlesinger. "Certified" $\mathrm{LiOH{\cdot}H_2O}$, $\mathrm{LiBr{\cdot}H_2O}$, and LiCl were from Fisher Chemical. $\mathrm{LiI{\cdot}3H_2O}$ ("purified") was from City Chemical Corp., N.Y. Reagent grade $\mathrm{Li_2CO_3}$ came from Allied Chemical. "AR" grade $\mathrm{H_3PO_4}$ (85%) was purchased from Mallinckrodt. Dowex 50W-X8 was obtained from Bio-Rad Laboratories, and 1,1,3,3-tetrabromoethane was from Mallinckrodt.

$\mathrm{Li_3PO_4}$ was prepared by mixing $\mathrm{LiOH{\cdot}H_2O}$ with a stoichiometric amount of 85% $\mathrm{H_3PO_4}$. The resulting $\mathrm{Li_3PO_4}$ was washed several times with deionized water and fired in a platinum dish to 500 °C. It was analyzed by titration with HCl, which showed the solid to be $\mathrm{Li_3PO_4{\cdot}0.02H_2O}$ (EW = 38.73 g).

$\mathrm{CePO_4}$ was prepared by reducing $\mathrm{CeO_2}$ with 47% HI (Mallinckrodt). The resulting solution was filtered and then treated with excess $\mathrm{H_3PO_4}$ (85%). Impure $\mathrm{CePO_4}$ precipitated. This was collected by filtration and purified three times by boiling an aqueous suspension of the solid for 1 h. The purified product was analyzed by X-ray powder diffraction[5] and by neutron activation analysis.

B. High-Temperature Experiments. In these experiments, the solid reactants were ground together and placed into a platinum boat, which was covered with Pt foil and introduced into a fused-quartz tube. A tube furnace was then used to heat the solids. A continuously flowing stream of Ar at essentially 1 atm pressure was used to purge air from the tube and to carry evolved gases away from the solids and into calibrated, continuously operating measurement devices—a Gow-Mac Model 20-150 thermal conductivity detector for $\mathrm{H_2}$ and a Beckman Model 741 oxygen analyzer. Steam was preheated to 220 °C and passed over the Pt boat at a rate equivalent to 3.2–4.8 mL of condensed $\mathrm{H_2O(l)}$/min. For reactions involving LiX's, the resulting HX was condensed with the steam from the Ar stream by a water-cooled condenser. The amounts of evolved HX were determined by titration with standardized NaOH. For reactions involving $\mathrm{Li_2CO_3}$, the resulting $\mathrm{CO_2(g)}$ was trapped in a solution of 2 N NaOH. In every case, a $\mathrm{CaSO_4}$ column was used to dry the $\mathrm{Ar{-}H_2}$ or $\mathrm{Ar{-}O_2}$ mixtures before they reached the gas-measuring devices.

A thermal controller was used to increase the reaction temperatures at a steady rate, usually about 5 °C/min. Solid products were characterized by X-ray powder diffraction[5] and by acid–base titration.

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Registry No. $\mathrm{CePO_4}$, 13454-71-2; LiCl, 7447-41-8; LiBr, 7550-35-8; LiI, 10377-51-2; $\mathrm{H_2O}$, 7732-18-5.

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Theoretical Prediction and Experimental Confirmation of Trans to Cis Photoisomerization in $\mathrm{d^6}$ Transition-Metal Complexes

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Experimental study of photosubstitution reactions

$$cis\text{-}[\mathrm{MA_4XY}] + \mathrm{S} \xrightarrow{h\nu} [\mathrm{MA_4XS}] + \mathrm{Y}$$

has led to the generalization that geometrical isomerization is often expected when M = $\mathrm{d^6}$ metal ion. The reasons for this recently have been given by Vanquickenborne and Ceulemans (V/C) in an angular overlap model (AOM) study.[1] Prior to their report, one of us had already discovered (and subsequently published[2]) that *cis*-$[\mathrm{Rh(en)_2(NH_3)Cl}]^{2+}$ did not fit the generalization, and we embarked on an AOM study of our own. Where they overlap, our independent calculations

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