

undergoes racemization at 100° C., and that this racemization process is catalysed by the cobalt(II) complex. The concentrations of the cobalt(III) complex and of the cobalt(II) complex have been varied, as has the ionic strength. The pH was maintained in the region 2.0 ± 0.2 . The expected pseudo-first-order kinetics in rotation were observed in accordance with the expression:

$$-\ln(\alpha/\alpha_0) = Rt$$

where α is the rotation at any time t , α_0 is the rotation at zero time, and R is the pseudo-first-order rate constant.

The integrated rate law accounting for these two paths is:

$$-\ln(\alpha/\alpha_0) = 2(kb + k')t$$

where k is the second-order constant associated with electron-transfer process, k' is the rate constant for thermal racemization, and b is the concentration of [Co-II (EDTA)]²⁻. Equating coefficients of t in the experimental and theoretical rate equations gives the equation:

$$R = 2kb + 2k'$$

From the linear dependence of R on b , k and k' are evaluated to be $1.4 M^{-1}hr^{-1}$ and $0.015 hr^{-1}$, respectively. Direct determination of k' also gives an average value of $0.015 hr^{-1}$ for five experiments involving zero concentration of cobalt(II) complex.

The results reported by Adamson and Vorres³ were determined at 60°, 70° and 85° C. Extrapolation of them to 100° C. gives $2.1 M^{-1}hr^{-1}$ as the value for the second-order rate constant. It can be shown that k , as defined here, corresponds to one-half the value derived from the McKay equation for electron transfer (isotopic method). Consequently, the value determined here ($1.4 M^{-1}hr^{-1}$) should be compared with one-half the value reported by Adamson and Vorres, namely, $1.1 M^{-1}hr^{-1}$. These studies will be reported in greater detail at a later date.

Support of this research by the National Science Foundation, Washington 25, D.C., is gratefully acknowledged.

YONG AE IM
DARYLE H. BUSCH

Department of Chemistry, Ohio State University,
Columbus, Ohio. Sept. 3.

¹ Dwyer, F. P., and Gyrfas, E. C., *Nature*, **166**, 481 (1950).

² Eichler, E., thesis, Washington University, St. Louis, Mo. (1955).
Wahl, A. C., Symposium on Mechanisms of Inorganic Reactions in Solution, Northwestern University, Evanston, Illinois, July 11, 1958.

³ Adamson, A. W., and Vorres, K. S., *J. Inorg. Nucl. Chem.*, **3**, 206 (1956).

⁴ Busch, D. H., and Bailar, jun., J. C., *J. Amer. Chem. Soc.*, **76**, 4574 (1953).

⁵ Dwyer, F. P., Gyrfas, E. C., and Mellor, D. P., *J. Phys. Chem.*, **59**, 296 (1955).

Electronic Configuration d^4 in a Complex Ion

BECAUSE of the instability of the valence states which transition metal atoms must possess in order to have four non-bonding electrons remaining after forming a d^2sp^3 octahedral complex ion, few simple ions of this configuration have been studied. This lack of experimental data has seriously hindered the elucidation of the properties to be expected for a complex ion of this type¹.

In this laboratory we have recently measured the magnetic susceptibilities of the potassium hexahalo-osmates-IV, K_2OsF_6 , K_2OsCl_6 and K_2OsBr_6 , and recorded their ultra-violet and visible spectra (200–

750 m μ) and their infra-red spectra (2–33 μ). Johannesan and Lindberg² previously reported that $(NH_4)_2OsBr_6$ exhibited a paramagnetism independent of temperature which they explained on the basis of Kotani's³ theory of spin-orbit coupling. Nyholm *et al.*⁴ have recently shown that the same ideas can be applied to K_2OsCl_6 . In both the above cases, a reasonably good agreement with theory is obtained for the magnetic properties of these compounds, if one invokes a rather large amount of spin-orbit coupling, $A = 6,400 cm^{-1}$.

We have found that this large amount of spin-orbit coupling will also explain the observed visible spectra for K_2OsCl_6 and K_2OsBr_6 when the predictions of Kotani's theory are combined with certain results from ligand field theory.

In Kotani's theory the spatial degeneracy of the three t_{2g} orbitals is removed, and the resulting levels have energies $-A/2$, $-A$, and $A/2 cm^{-1}$ respectively. If one considers transitions from these 'perturbed' levels to an anti-bonding e^*_g orbital, the counterpart of the bonding molecular orbital constructed from the d_{eg} orbital of metal atom and the e_g orbital of the ligand, a reasonable explanation of the absorption spectra results. One finds peaks which differ in energies by approximately the amounts which the t_{2g} orbitals are perturbed via spin-orbit coupling. The energy difference between the lowest t_{2g} orbital and the e^*_g orbital (10 Dq) decreases regularly from OsF_6^{2-} to $OsBr_6^{2-}$, as one would predict due to the decreasing strength of the crystal fields.

Unfortunately, the magnetic results obtained for K_2OsF_6 do not fit a Kotani-type curve, and hence it is difficult to evaluate the spin-orbit coupling constant. It is interesting to note that the visible spectrum of this material differs markedly from that of the others, containing only two bands, one at 50,000 cm^{-1} and one at 32,467 cm^{-1} ⁵, and also that this material is a light yellow compound while K_2OsCl_6 (wine-red) and K_2OsBr_6 (black) are both deeply coloured materials.

It would be interesting to see if other complex ions of the heavier transition metal atoms possess an absorption spectrum which can be explained by the utilization of the spin-orbit coupling concept. These three materials, together with $(NH_4)_2OsBr_6$, are (to our knowledge) the only known examples of paramagnetic substances independent of temperature among the complex ions of the platinum group elements.

The details of the above work and a more complete discussion of the theoretical aspects of the problem will be published soon.

We would like to acknowledge the many helpful discussions with Dr. James Richardson and Dr. J. M. Honig. One of us (A. G. T.) wishes to acknowledge the financial assistance of the Purdue Research Foundation and the Research Corporation for the years 1956 and 1957.

ALMON G. TURNER, JUN.
ALAN F. CLIFFORD

Department of Chemistry,
Purdue University,
Lafayette, Indiana.
Sept. 16.

¹ Orgel, L. E., *J. Chem. Phys.*, **23**, 1004 (1955).

² Johannesan, R. B., and Lindberg, A. R., *J. Amer. Chem. Soc.*, **76**, 5349 (1954).

³ Kotani, M., *J. Phys. Soc. Japan*, **4**, 293 (1949).

⁴ Nyholm, R. S., *et al.*, *Nature*, **179**, 1121 (1957).

⁵ Hepworth, M. A., Robinson, P. L., and Westland, G. J., *J. Chem. Soc.*, 611 (1958).