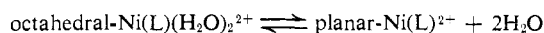


Rapid Planar–Octahedral Interconversion with Nickel(II) Complexes

Sir:

Yellow or brown diamagnetic planar and blue-violet paramagnetic octahedral are both well-established forms for nickel(II). With certain polyamine complexes, both conformations exist in solution in detectable concentrations. Thus, blue aqueous solutions containing $\text{Ni}(\text{trien})(\text{H}_2\text{O})_2^{2+}$, $\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2^{2+}$, or $\text{Ni}(\text{pn})_2(\text{H}_2\text{O})_2^{2+}$ turn brownish yellow on heating. The absorption band at $\sim 440 \text{ m}\mu$ characteristic of tetragonal nickel(II) is developed, and the original color returns on cooling the solution.^{1,2} Aqueous solutions of the nickel complex of the quadridentate ligand $\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}_2$ (abbreviated 2,3,2-tet) are already brown³ and thus contain substantial amounts of the planar form at room temperature.⁴ Information on the rate at which such equilibria as ($L = \text{trien}$, or 2,3,2-tet)

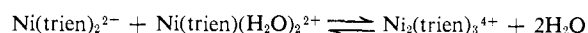
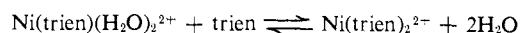


are established is lacking, but the system is amenable to the relaxation method of rate measurement.⁵ Sizable absorbance changes at $440 \text{ m}\mu$ with a small temperature rise, $2.5\text{--}6.5^\circ$, particularly with the 2,3,2-tet complex, allowed work at low amplification and thus at the shortest time ranges of the temperature-jump apparatus.⁵ It was found, however, that with the 1:1 nickel(II)–trien and nickel(II)–2,3,2-tet systems, the establishment of the yellow–blue equilibria was complete at 5° within $10 \mu\text{sec}$ which was the shortest time we could reach with our equipment. The first-order rate constant for the conformation change must be $>10^5 \text{ sec}^{-1}$. Only a slight “electronic ripple” was observed when solutions of $\text{Ni}(\text{tren})(\text{H}_2\text{O})_2^{2+}$ or KNO_3 were used in the temperature-jump cell. The amine tren, $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$, can only coordinate to leave two *cis* positions in the octahedron.

We believe that with 2,3,2-tet the fast transition observed is between the *trans*-octahedral and the planar complex. Of relevance are the reactions of the complex with EDTA and oxalate which indicate that there are at least two blue isomers of $\text{Ni}(2,3,2\text{-tet})(\text{H}_2\text{O})_2^{2+}$ present in solution. Upon mixing EDTA and Ni –2,3,2-tet (1:1) complex there is an absorbance jump at $380 \text{ m}\mu$ corresponding to about 40% of the total complex present, the remainder, both blue and yellow forms, reacting by a slow first-order process ($k = 9.3 \times 10^{-4} \text{ sec}^{-1}$ at pH 8.34).⁶ The fast transition with the trien complex may be due to a *trans*-octahedral–planar equilibrium although $\text{Ni}(\text{trien})(\text{H}_2\text{O})_2^{2+}$ is believed to have predominantly the *cis*-octahedral structure in aqueous

solution.¹ The high rate constant resembles that noted for the planar, tetrahedral change observed with certain nickel(II) complexes,⁷ but it would be surprising if the rapid interconversion were between a square-planar and a *cis*-octahedral form of the tetramine. The structure of the yellow complex $\text{Ni}(\text{trien})(\text{ClO}_4)_2$ has recently been determined⁸ and shown to be square-planar with the Ni–N bond distances ($1.9\text{--}2.0 \text{ \AA}$) in good agreement with those determined for another square-planar nickel complex.⁹ These bond lengths are shorter than those in typical octahedral nickel complexes ($2.1\text{--}2.2 \text{ \AA}$),⁹ and therefore the high intramolecular rate constant observed is a little unexpected.

A previously reported¹⁰ relaxation time of about 5 msec observed in temperature-jump experiments on $\text{Ni}(\text{trien})(\text{H}_2\text{O})_2^{2+}$ is probably due to a slight excess of trien present in solution.¹¹ Indeed in the presence of an indicator (phenol red) it is possible to observe⁶ two relaxations in the time range 1–10 msec which are associated with the equilibria



In the absence of the indicator, the rapidly established planar \rightleftharpoons octahedral system would act as a type of indicator for the above equilibria.

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(7) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Amer. Chem. Soc.*, **85**, 397 (1963).

(8) A. McPherson, M. G. Rossman, D. W. Margerum, and M. R. James, submitted for publication.

(9) S. C. Nyburg and J. S. Wood, *Inorg. Chem.*, **3**, 468 (1964).

(10) R. G. Wilkins cited in M. Eigen, *Ber. Bunsenges. Phys. Chem.*, **67**, 753 (1963).

(11) The trien used in these early experiments was not purified and the nickel–trien proportions were not carefully controlled.

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The Structures of Pentacarbonyltriphenylphosphinechromium and Pentacarbonyl(triphenyl phosphite)chromium

Sir:

The occurrence of π bonding between metals and phosphorus ligands has been widely accepted for more than a decade,¹ although recently this subject has become rather controversial.^{2–4} Of particular interest have been compounds of the type $\text{LM}(\text{CO})_5$ where L is an amine, phosphine, arsine, etc., and M is chromium, molybdenum, or tungsten. The most voluminous data bearing on the subject are infrared car-

(1) F. A. Cotton and G. Wilkinson, “Advanced Inorganic Chemistry,” 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1966, pp 719–759.

(2) R. J. Angelici and M. D. Malone, *Inorg. Chem.*, **6**, 1731 (1967).

(3) L. M. Venanzi, *Chem. Brit.*, 162 (1968).

(4) R. E. Dessy and L. Wiczorek, submitted for publication.

(1) C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 399 (1957).

(2) K. Sone and M. Kato, *Z. Anorg. Allgem. Chem.*, **301**, 277 (1959).

(3) B. Bosnich, R. D. Gillard, E. D. McKenzie, and G. A. Webb, *J. Chem. Soc., A*, 1331 (1966).

(4) However, in aqueous solution (25° , $\mu = 0.5 \text{ M}$) the yellow form of $\text{Ni}(2,3,2\text{-tet})^{2+}$ cannot be more than 25% of the total $\text{Ni}(2,3,2\text{-tet})^{2+}$ as opposed to 50% suggested in an earlier report.⁵ This estimate is based on spectral measurements, using an approximate value for the molar absorptivity of the yellow form at $440 \text{ m}\mu$ of 67 (obtained in high electrolyte concentration, 7.4 M NaClO_4). The planar yellow form is at most 2% of the total $\text{Ni}(\text{trien})^{2+}$ under the conditions $\mu = 0.5 \text{ M}$, 25° .

(5) M. Eigen and L. De Maeyer in “Investigation of Rates and Mechanisms of Reactions,” Vol. VIII, Part II, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., of “Technique of Organic Chemistry,” Interscience Publishers, New York, N. Y., 1963, Chapter 18.

(6) D. W. Margerum and D. C. Weatherburn, work in progress.