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 $\mathrm{Ni(trien)(H_2O)_2}^{2+}$, $\mathrm{Ni(en)_2(H_2O)_2}^{2+}$, or $\mathrm{Ni(pn)_2(H_2O)_2}^{2+}$ turn brownish yellow on heating. The absorption band at ~440 mμ 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 $\mathrm{NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2}$ (abbreviated 2,3,2-tet) are already brown[3] and thus contain substantial amounts of the planar form at room temperature.[4] Information on the rate at which such equilibria as (L = trien, or 2,3,2-tet)

$$\text{octahedral-Ni(L)(H}_2\text{O)}_2{}^{2+} \rightleftharpoons \text{planar-Ni(L)}^{2+} + 2\mathrm{H_2O}$$

are established is lacking, but the system is amenable to the relaxation method of rate measurement.[5] Sizable absorbance changes at 440 mμ with a small temperature rise, 2.5–6.5°, 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 μsec which was the shortest time we could reach with our equipment. The first-order rate constant for the conformation change must be $>10^5$ sec^{-1}. Only a slight "electronic ripple" was observed when solutions of $\mathrm{Ni(tren)(H_2O)_2}^{2+}$ or $\mathrm{KNO_3}$ were used in the temperature-jump cell. The amine tren, $\mathrm{N(CH_2CH_2NH_2)_3}$, 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 $\mathrm{Ni(2,3,2\text{-}tet)(H_2O)_2}^{2+}$ present in solution. Upon mixing EDTA and Ni–2,3,2-tet (1:1) complex there is an absorbance jump at 380 mμ corresponding to about 40% of the total complex present, the remainder, both blue and yellow forms, reacting by a slow first-order process ($k = 9.3 \times 10^{-4}$ sec^{-1} at pH 8.34).[6] The fast transition with the trien complex may be due to a *trans*-octahedral–planar equilibrium although $\mathrm{Ni(trien)(H_2O)_2}^{2+}$ 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 $\mathrm{Ni(trien)(ClO_4)_2}$ has recently been determined[8] and shown to be square-planar with the Ni–N bond distances (1.9–2.0 Å) 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 (2.1–2.2 Å),[9] and therefore the high intramolecular rate constant observed is a little unexpected.

A previously reported[10] relaxation time of about 5 msec observed in temperature-jump experiments on $\mathrm{Ni(trien)(H_2O)_2}^{2+}$ 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 observe[6] two relaxations in the time range 1–10 msec which are associated with the equilibria

$$\mathrm{Ni(trien)(H_2O)_2}^{2+} + \text{trien} \rightleftharpoons \mathrm{Ni(trien)_2}^{2+} + 2\mathrm{H_2O}$$

$$\mathrm{Ni(trien)_2}^{2+} + \mathrm{Ni(trien)(H_2O)_2}^{2+} \rightleftharpoons \mathrm{Ni_2(trien)_3}^{4+} + 2\mathrm{H_2O}$$

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

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

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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 $\mathrm{LM(CO)_5}$ 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-

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