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 $\text{Ni(trien)(H}_2\text{O)}_2{}^{2+}$, $\text{Ni(en)}_2\text{(H}_2\text{O)}_2{}^{2+}$, or $\text{Ni(pn)}_2\text{(H}_2\text{O)}_2{}^{2+}$ 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 $\text{NH}_2\text{(CH}_2\text{)}_2\text{NH(CH}_2\text{)}_3\text{NH(CH}_2\text{)}_2\text{NH}_2$ (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)

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

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 $\text{Ni(tren)(H}_2\text{O)}_2{}^{2+}$ or KNO_3 were used in the temperature-jump cell. The amine tren, $\text{N(CH}_2\text{CH}_2\text{NH}_2\text{)}_3$, 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 $\text{Ni(2,3,2-tet)(H}_2\text{O)}_2{}^{2+}$ present in solution. Upon mixing EDTA and Ni–2,3,2-tet (1:1) complex there is an absorbance jump at 380 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 $\text{Ni(trien)(H}_2\text{O)}_2{}^{2+}$ 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 $\text{Ni(trien)(ClO}_4\text{)}_2$ 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 $\text{Ni(trien)(H}_2\text{O)}_2{}^{2+}$ 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 observe[6] two relaxations in the time range 1–10 msec which are associated with the equilibria

$$\text{Ni(trien)(H}_2\text{O)}_2{}^{2+} + \text{trien} \rightleftharpoons \text{Ni(trien)}_2{}^{2+} + 2\text{H}_2\text{O}$$

$$\text{Ni(trien)}_2{}^{2+} + \text{Ni(trien)(H}_2\text{O)}_2{}^{2+} \rightleftharpoons \text{Ni}_2\text{(trien)}_3{}^{4+} + 2\text{H}_2\text{O}$$

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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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 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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bonyl stretching frequencies and force constant data,[2,4-7] although other types of data have been presented, such as equilibrium constants,[8] metal–ligand and metal–carbon stretching frequencies,[9] and phosphorus–tungsten coupling constants.[10,11] To date, however, there has been no comparison of two or more molecular structures of similar compounds (*e.g.*, $LCr(CO)_5$ and $L'Cr(CO)_5$, where L and L′ are different phosphorus ligands) in which the π-bonding ability of the ligands are different.

We report here the preliminary results of such a study in which triphenylphosphine and triphenyl phosphite were chosen as the ligands because they have been shown to have somewhat different bonding properties in $LM(CO)_5$ as determined from infrared spectra and tungsten–phosphorus coupling constant data.[11]

Crystals of pentacarbonyltriphenylphosphinechromium and pentacarbonyl(triphenyl phosphite)chromium are triclinic, $P\bar{1}$, with two formula units in the cell. The phosphine complex, $(C_6H_5)_3PCr(CO)_5$, has cell dimensions $a = 9.7086 \pm 0.0031$, $b = 11.9419 \pm 0.0020$, $c = 9.5519 \pm 0.0027$ Å, $\alpha = 91.733 \pm 0.018°$, $\beta = 95.583 \pm 0.038°$, $\gamma = 74.167 \pm 0.015°$; and the phosphite complex, $(C_6H_5O)_3PCr(CO)_5$, has cell dimensions $a = 11.2118 \pm 0.0035$, $b = 11.4971 \pm 0.0044$, $c = 10.6950 \pm 0.0029$ Å, $\alpha = 114.333 \pm 0.039°$, $\beta = 105.583 \pm 0.028°$, $\gamma = 66.500 \pm 0.018°$. Data for both structures were measured to a 2θ of 55° with a General Electric XRD-6 automated diffractometer using niobium-filtered molybdenum radiation (λ 0.71069) and the θ–2θ scan technique. The structure of the phosphine compound was solved by Patterson and Fourier methods[12] and refined to an R value of 0.043 by least-squares on 4885 reflections. The structure of the phosphite compound was solved by statistical and Fourier methods[12] and refined to an R value of 0.052 on 5263 reflections. The hydrogen atom positions for both structures were assumed from known benzene geometry and refined with isotropic temperature factors.

The salient structural features of these compounds are given in Table I. The phosphorus and five carbonyls form an approximate octahedron about chromium, with one carbonyl *trans* to phosphorus and the other four carbonyls *cis* to phosphorus. The π-bonding theory predicts that the *trans* Cr–C distance should be significantly shorter than the *cis* Cr–C distances, and concomitantly that the *cis* C–O distances should be shorter than the *trans* C–O distance. This is indeed observed in each compound. Furthermore, the infrared spectra of these compounds and $^{183}W-^{31}P$ coupling (411 Hz for the phosphite and 280 Hz for the phosphine complex)[11] in the analogous tungsten compounds suggests, according to the π theory, that triphenyl phosphite is a better π acceptor than triphenylphosphine.[13,14]

Table I

Bond	Bond length, Å Phosphite	Phosphine
Cr–P	2.309 (1)	2.422 (1)
Cr–C (*trans*)	1.861 (4)	1.844 (4)
C–O (*trans*)	1.136 (6)	1.154 (5)
Cr–C (*cis*, av)	1.896 (4)	1.880 (4)
C–O (*cis*, av)	1.131 (6)	1.147 (6)

Consequently, it is expected that for the phosphite complex the Cr–P distance should be shorter, the *trans* Cr–C bond should be longer, the *trans* C–O bond should be shorter, the *cis* Cr–C bond should be longer, and the *cis* C–O distance should be shorter than the respective distances in the triphenylphosphine complex. Remarkably, all these expectations are experimentally confirmed. The π-bonding theory[5,6] also predicts that changes in the π-acceptor ability of the ligand should effect the *trans* CO about twice as much as the *cis* CO's due to the symmetry and number of metal d orbitals involved in the bonding. However, the differences in both the *cis* and *trans* Cr–C and C–O bond lengths between the phosphite and phosphine complexes are roughly equivalent.

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Trimethylsilylmercury Complexes[1]

Sir:

The recent communication[2] on the possible intermediacy of methylmercury complexes in the exchange between methyllithium and dimethylmercury in ether and THF (tetrahydrofuran) prompts us to report our observations on timethylsilylmercury complexes.

We have prepared a series of highly colored compounds (Table I) containing tristrimethylsilylmercury or tetrakistrimethylsilylmercury complexes by the reactions

$$LiSiMe_3 + Hg(SiMe_3)_3 \xrightarrow{DME} LiHg(SiMe_3)_3$$

$$2LiSiMe_3 + Hg(SiMe_3)_2 \xrightarrow[\text{or } C_5H_{10}]{DME} Li_2Hg(SiMe_3)_4$$

$$2Na\,[K] + 2Hg(SiMe_3)_2 \xrightarrow[C_5H_{10}]{} Na_2Hg(SiMe_3)_4\;[\text{or } K_2Hg(SiMe_3)_4]$$

The decrease in the $^{199}Hg-^{1}H$ coupling constant from the bis- to the tetrakistrimethylsilylmercury compounds is similar to that observed for increasing alkyl substitution in other organometallic compounds.[3] If a

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