have been expected on the basis of VSEPR alone since, even considering the directional character of the π-bonding electrons in the Cl=O double bond,[9] the oxygen should better be able to compete with the lone pair for equatorial space about the chlorine atom. Rather, the OClF angle closes down from a Bent's rule effect just as the FSF angle in SF_4 does. *However*, in $OClF_3$ the difference in electronegativity between the central chlorine atom and the substituent oxygen and fluorine atoms is considerably less (Δ_χ = ca. 0.6) than that between the central sulfur atom and the substituent fluorine atoms ($\Delta_\chi = 1.4$); therefore the angle trans to the lone pair closes only to 108.9° rather than to 101°. In contrast, the opening of the OClF angle to 94.7° (expected = 90°) *contrary* to Bent's rule is conclusive proof of the directional nature of the π interaction espoused by Christe and Oberhammer.

In summary, for isovalent hybridization of X–Y–Z systems, the more closely the electronegativities of X and Z match, the more important will be the covalent contribution to *both* bonds and the more nearly equal will be the s character of the two hybrid orbitals on atom Y. For Z much more electronegative than X, s character will tend to reside in the X-directed orbital and the easily ionized p character will be directed to the more highly ionic X-Z bond. Furthermore, differences in electronegativity between the central atom and the peripheral atoms are probably more important than the absolute electronegativity of the latter.

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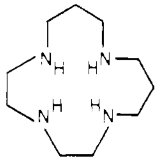
Coordination Behavior of the Tetraaza Macrocycle Isocyclam

Sir:

In a paper from this laboratory,[1] the synthesis of the 14-membered saturated tetraaza macrocycle isocyclam (1,4,7,11-tetraazacyclotetradecane (I)) as well as its coordinative behavior against the nickel(II) ion was described. Compounds containing both low-spin square-planar and high-spin pseudooctahedral nickel(II) chromophores were isolated, and both four- and six-coordinate species were found to coexist in aqueous solution according to a temperature-dependent equilibrium. For all of these nickel(II)–isocyclam moieties it was suggested that the ligand was planarly arranged around the metal ion, thus behaving as tetradentate.



I

More recently further work has been reported on the same subject by Blinn and co-workers.[2] They claim that in the square-planar nickel(II) derivatives only three nitrogen donors are bound to the metal ion with the uncoordinated fourth one potentially behaving as a Brønsted base in aqueous solution. This hypothesis is surprising for several reasons: (i) the stabilization of the singlet ground state of nickel(II) ion, in absence of steric effects,[3] is usually achieved through the coordination of four amine nitrogen donors; (ii) the exothermic heat of complex formation of metal ion–polyamine systems reflects the exothermic formation of metal–nitrogen coordination bonds,[4] and calorimetric investigations performed in this laboratory have recently shown[5] that the formation of the low-spin $[Ni(isocyclam)]^{2+}$ species is remarkably more exothermic than that of the homologous species with the corresponding 13-membered macrocycle. X-ray diffractometric studies have shown that in the latter compound the ligand acts as tetradentate.[6] Also, the formation of the nickel(II) complex with the isocyclam ligand is also more exothermic than that with the open-chain tetraamine trien, which surely acts as tetradentate.[7]

All of the above considerations strongly suggest that the isocyclam is fully coordinated to the metal ion in the low-spin complex, and we feel that Blinn and co-workers hypothesis on the tridentate behavior of the isocyclam is based on questionable experimental data. For example, they speculate on the increase of the pH value which they found to follow the dissolution in water of some solid complexes (but with no figures reported). Since the acidic or basic character of chemical species in aqueous solution can be clearly evidenced through a pH titration, we have performed the following experiments: two 10^{-2} M solutions of hydrochloric acid, one containing an equimolar amount of $Ni(isocyclam)(ClO_4)_2$, were potentiometrically titrated with a standard base. Two superimposable titration curves were obtained, without any inflection which would indicate the existence of some acid–base equilibria involving the macrocyclic moiety. It is well-known that, when a relatively pure material is dissolved in water, a pH change may occur as a consequence of the presence of basic or acidic impurities. It seems likely that this is the source of Blinn's pH effect.

Furthermore, Blinn and co-workers also investigated the octahedral–square-planar equilibrium which occurs, as mentioned above, in aqueous solution (eq 1). They confirm the

$$[Ni(isocyclam)(H_2O)_2]^{2+} \rightleftharpoons [Ni(isocyclam)]^{2+} + 2H_2O \qquad (1)$$

findings and thermodynamic quantities previously obtained in our laboratory. If in the low-spin complex one nitrogen donor were free and behaved as a base, as they proposed, addition of acid would displace equilibrium 1 to the right, favoring the formation of the low-spin species. A neutral aqueous solution of $Ni(isocyclam)(ClO_4)_2$ containing 60% of the low-spin species, as monitored by the intensity of the band at 463 nm, was spectrophotometrically titrated with standard acid. It was found that the progressive decrease of the pH (down to 2) did not involve any increase or decrease of the low-spin species.

Further information on the nature of the chromophores involved in equilibrium 1 is provided by the ^1H NMR of D_2O solutions of nickel(II)–isocyclam derivatives. The NMR traces consist of ten resonances, eight located downfield and two upfield as referenced to DSS standard. With the existence of equilibrium 1, involving both diamagnetic and paramagnetic chromophores, the observed pattern of resonances is very similar to that found for $CDCl_3$ solutions containing the fully paramagnetic $Ni(isocyclam)Cl_2$ complex[8] and unambiguously

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(1) Sabatini, L.; Fabbrizzi, L. *Inorg. Chem.* **1979**, *18*, 438.

(2) Swisher, R. G.; Dayhuff, J. P.; Stuher, D. J.; Blinn, E. L. *Inorg. Chem.* **1980**, *19*, 1336.

(3) Patel, B. N.; Billo, E. J. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 335.

(4) Fabbrizzi, L.; Micheloni, M.; Paoletti, P. *Inorg. Chem.* **1980**, *19*, 535 and references therein.

(5) Fabbrizzi, L.; Micheloni, M.; Paoletti, P. *J. Chem. Soc., Dalton Trans.* **1980**, 134.

(6) Waters, J. M.; Whittle, K. R. *J. Inorg. Nucl. Chem.* **1972**, *34*, 115.

(7) McPherson, A. C.; Rossmann, M. G.; Margerum, D. W.; James, M. R. *J. Coord. Chem.*, **1971**, *1*, 39.

(8) Dei, A., to be submitted for publication.

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indicates a tetradentate behavior of the ligand in the trans-octahedral chromophore. For this compound the observed spectral features are clearly consistent with C_s symmetry in which the five- and six-membered chelate rings have gauche and chair conformations, respectively. No changes were observed in the NMR spectrum as the pD was lowered which confirms our earlier conclusion that Ni(isocyclam)$^{2+}$ is not involved in acid–base equilibria.

In conclusion, we feel that the available data are only consistent with tetradentate behavior for the isocyclam ligand in its nickel(II) complexes and that there is no basis for the claim that it is tridentate in the diamagnetic species.

Registry No. I, 52877-36-8; [Ni(isocyclam)]$^{2+}$, 46365-93-9; [Ni(isocyclam)(H$_2$O)$_2$]$^{2+}$, 68317-92-0; [Ni(isocyclam)](ClO$_4$)$_2$, 68344-01-4.

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Electron-Transfer Catalysis of Substitution

Sir:

In describing[1] our results on chiral discrimination in outer-sphere electron-transfer reactions, we neglected an important set of results which are germane to our case. Busch et al.[2] report that when (−)-Co(*d*-PDTA)$^-$ reacts with ethylenediamine, Co(en)$_3^{3+}$ is formed with a large excess of one chiral form over the other. Detailed observations were not given nor do they appear in either of two subsequent papers.[3,4] However, in ref 2 it is stated that in the first experiment (50% en at 25 °C) "complete retention of generic configuration" was observed. Further, that in attempts to reproduce the experiment, random results were obtained. A more detailed account of reaction conditions is given by Irving and Gillard[5] in reporting on the same reaction. In ~25% en in water at 25 °C, reaction was found to be essentially complete in 12 min producing Co(en)$_3^{3+}$ which showed an optical rotatory power ca. 90% that of a pure enantiomer.

The purpose of this communication is to point out that the rapid reaction reported by Irving and Gillard[5] does not correspond to direct substitution but that instead an electron-transfer process carries the reaction.

We find, just as has been reported,[5] that the reaction between en and Co(PDTA)$^-$ is complete in a matter of minutes (our conditions differed from those of I and G only in that we used 50% en in water). The reaction is accelerated by Co^{2+}, but when H$_2$O$_2$ is present, the half-life is longer than 2 h. Reaction does eventually set in, but of course H$_2$O$_2$ is in time consumed by en.

Our interest has extended also to the kinetic data reported by Busch et al.[4] In attempting to reproduce the results of some of their experiments, (pH 10, 35 °C; see Table II of ref 4) we find, as they reported, that the reaction is first order in Co(PDTA)$^-$. However, our values of k_{obsd} are smaller than theirs by almost a factor of 2, and we observe a short induction period in the reaction. Moreover, when $S_2O_8^{2-}$ at ~10^{-2} M is present, the rates are decreased by a factor of at least 10 and by an even larger factor when H$_2$O$_2$ is added. When argon is passed through the reaction mixture, the rates of reaction are increased. We infer therefore that the kinetics reported[4] apply to the reaction of Co(PDTA)$^-$ with en as catalyzed by Co^{2+}. We infer furthermore that Co^{2+} is not necessarily adventitious but that it is maintained at a steady state, being produced by the reduction of Co(III) by en and scavenged by O$_2$. At any rate, we believe that the intrinsic rate of the direct reaction of en with Co(PDTA)$^-$ was not being studied by Busch et al.[4]

From these observations, we conclude that the results on retention of chirality which have been reported apply to the reaction catalyzed by Co^{2+}; i.e., they speak to chiral discrimination in the reaction of Co(PDTA)$^-$ with Co(en)$_3^{2+}$ and *not* to direct replacement of PDTA by en as has been assumed. It is obvious that the large degree of discrimination has important implications as to the detailed geometry of the activated complex for electron transfer.

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Registry No. (−)-Co(*d*-PDTA)$^-$, 78854-20-3; en, 107-15-3.

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(1) Geselowitz, D. A.; Taube, H. *J. Am. Chem. Soc.* **1980**, *102*, 4525.
(2) Busch D. H.; Cooke, D. W.; Swaminathan, K.; Im, Y. A. "Advances in the Chemistry of Coordination Compounds"; Macmillan: New York, 1961; p 139.
(3) Busch, D. H.; Swaminathan, K. *J. Inorg. Nucl. Chem.* **1961**, *23*, 150.
(4) Busch, D. H.; Swaminathan, K.; Cooke, D. W. *Inorg. Chem.* **1962**, *1*, 260.
(5) Irving, H.; Gillard, R. D. *J. Chem. Soc.* **1961**, 2249.

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Catalytic Isomerization of Alkenes by Palladium(II) Compounds. An Alternative Mechanistic View

Sir:

The catalytic isomerization of alkenes by Pd(II) compounds, especially Pd(PhCN)$_2$Cl$_2$ (**1**), has been the subject of a number of mechanistic studies.[1] The commonly postulated mechanism involves the oxidative addition of an allylic C–H bond to the Pd(II) catalyst to produce a palladium(IV) allyl hydride species, **2**, as outlined in Scheme I(A). However, Pd(IV) constitutes a rare and unstable oxidation state for palladium,[2] and in view of the pronounced electrophilicity of Pd(II) compounds which lack strongly basic ligands (e.g., PR$_3$),[3] such an oxidative addition step appears unlikely. Moreover, we have observed that the catalytic isomerization of alkenes proceeds

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(1) (a) Harrod, J. F.; Chalk, A. J. *J. Am. Chem. Soc.* **1966**, *88*, 3491. (b) Cramer, R.; Lindsey, R. V. *Ibid.* **1966**, *88*, 3534. (c) Bingham, D.; Hudson, B.; Webster, D. E.; Wells, P. B. *J. Chem. Soc., Dalton Trans.* **1974**, 1521.
(2) Hartley, F. R. "The Chemistry of Platinum and Palladium"; Wiley: New York, 1973.
(3) For numerous examples attesting to the electrophilicity of Pd(II) compounds, see: Tsuji, J. "Organic Synthesis with Palladium Compounds"; Springer-Verlag: New York, 1980.