added where, contrary to earlier reports, we find the product of the interaction to be quite soluble.

Taking into account the stoichiometry of the reaction producing the new species, its spectrum, its cation-exchange behavior, and the magnetic susceptibility, we conclude that the dominant form must be formulated as Rh_2^{4+}. The hydrated ion is presumably $Rh_2(H_2O)_8(H_2O')_2^{4+}$, but the supposition as to its formula awaits confirmation by isotopic studies. These are planned, and further work on the properties of the new species is in progress. Important in this program are more detailed studies of the magnetic susceptibility which indicates that the equilibrium

$$Rh^{4+} = 2Rh^{2+}$$

is a significant aspect of the behavior of the system.

In view of the existence[14] of binuclear carboxylates of Mo(II), it seems likely that an aquo ion analogous to that described for Rh(II) exists for molybdenum as well.

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(14) T. A. Stephenson and G. Wilkinson, *J. Chem. Soc.*, 2538 (1964).
(15) On leave from Università di Roma.

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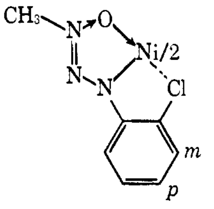
Coordination by the Chloro Group. Intramolecular Planar ⇌ Octahedral Equilibrium in a Nickel Complex

Sir:

A novel example of the intramolecular solution equilibrium[1]

$$\text{planar } (S = 0) \rightleftharpoons \text{octahedral } (S = 1) \qquad (1)$$

is provided by the substituted triazene 1-oxide[2] chelate of Ni(II), **1** (the dotted line is used to indicate that the chlorine atom may ($S = 1$) or may not ($S = 0$) be coordinated). Intramolecular equilibria of this kind are known in a few cases, *e.g.*, in some salicylaldimines.[4] However, none of these involves halogen coordination. The chloro group attached to a benzene ring will normally be recognized as a very poor donor. The uniqueness of **1** lies in this group demonstrably acting as a labile coordination site for Ni(II).



1

The olive-green complex **1** is synthesized by reacting the ligand[5] with nickel acetate in aqueous alcoholic solution. In Nujol mull, it shows only one electronic band in the visible region at 710 mμ. It is diamagnetic and hence planar in the crystalline state. However, its greenish brown solution in chloroform is "partially" paramagnetic, the magnetic moment[6] being ~2 BM at 32°. The solution shows two electronic bands at 725 and 1095 mμ having molar extinction coefficients (ϵ) of 62 and 24 l. mole^{-1} cm^{-1}, respectively. The behavior of **1** in benzene solution is similar except that the concentration of the triplet species is appreciably less. In this solvent, the 1095-mμ band strictly follows Beer's law in the concentration range 0.005–0.05 *M*. The osmometric (37°) molecular weight of **1** in benzene is 434 (calcd 428).

These data strongly suggest the existence of equilibrium 1 in the above solutions. In chloroform solution, many planar Ni(II) chelates of triazene 1-oxides show a singlet–singlet band at ~730 mμ (ϵ ~110).[7] On this basis, the observed ϵ (725 mμ) of **1** suggests a ~57% population of the singlet state at 32°. If the reasonable[4] assumption is made that the octahedral form of **1** has a magnetic moment of ~3.2 BM, the observed moment (2 BM) agrees reasonably well[8] with the above population. The 1095-mμ band is assigned to the $^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1) transition[9] assuming effective octahedral symmetry for the triplet species. In nickel complexes having strict O_h symmetry, ν_1 generally has[10] $\epsilon < 5$. The relatively high intensity in the present case is indicative of considerable deviation from O_h symmetry.[11] A parallel situation exists in some other hexacoordinated nickel chelates derived from tridentate ligands.[4]

An important evidence in favor of coordination by the chloro group in **1** is provided by the observation that the corresponding chelates having a chloro group in *meta* or *para* position show no spectral or magnetic evidence for any appreciable population of the triplet state, *e.g.*, the *m*-chloro complex shows only a singlet–singlet band at 730 mμ (ϵ 110) in benzene. In these cases *intramolecular* chloro coordination is not possible

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(1) The words "planar" and "octahedral" are not used in strict sense.
(2) This formulation is supported by ir data.[3]
(3) T. Mitsuhasi, Y. Osamura, and O. Simamura, *Tetrahedron Letters*, 2593 (1965); A. Chakravorty, B. Behera, and P. S. Zacharias, *Inorg. Chim. Acta*, 2, 85 (1968).
(4) A. Chakravorty, J. P. Fennessey, and R. H. Holm, *Inorg. Chem.*, 4, 26 (1965); L. Sacconi, P. Nannelli, and U. Campigli, *ibid.*, 4, 818 (1965); L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *ibid.*, 4, 1943 (1965); L. Sacconi, N. Nardi, and F. Zanobini, *ibid.*, 5, 1872 (1966).
(5) S. M. Dugar and N. C. Sogani, *J. Indian Chem. Soc.*, **43**, 289 (1966).
(6) Measurements were done by an nmr method: D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
(7) B. Behera and A. Chakravorty, submitted for publication.
(8) % planar species = $\{1 - (2^2/(3.2)^2)\} \times 100 \approx 61$.
(9) Of the other two crystal-field transitions, *viz.* $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3), ν_3 is most probably hidden under the tail of an intense allowed transition (340 mμ (ϵ ~ 9000)) centered mainly in the ligand. We did not get any direct evidence for ν_2 (expected in the 600–700-mμ region) either. However we strongly suspect that it is hidden under the envelope of the relatively intense 725-mμ band of the singlet species. Strong supporting evidence is provided by the methoxyl analog (*i.e.*, OCH_3 in place of Cl in 1). In benzene or chloroform solution, this monomeric chelate is ~100% in the octahedral triplet state (methoxyl coordination). Two broad bands at 1180 and 690 mμ are observed. These are assignable to ν_1 and ν_2, respectively. The shape of the 1180-mμ band is very similar to that of the 1095-mμ band of **1**.
(10) C. K. Jørgensen, *Acta Chem. Scand.*, 10, 887 (1956).
(11) We believe that the tridentate ligand in 1 is meridionally disposed in the octahedral configuration. The resulting *cis* geometry has no center of symmetry. In addition to intensification, this may cause splitting of bands. We have evidence that the 1095-mμ absorption consists of at least two overlapping components. The possibility that the high-spin chelate is five-coordinated (coordination by only one of the chloro groups) was considered. However, the balance of spectral evidence favors six-coordination.

for obvious reasons. Chloro coordination in **1** results from a *compelling* steric disposition of the chloro group. Thus a solution of the unsubstituted chelate (*i.e.*, H in place of Cl in **1**) in chlorobenzene shows *no* evidence for population of the triplet state brought about by *intermolecular* chloro coordination.

The bromo compound corresponding to **1** behaves in the same way except that the equilibrium concentration of the octahedral species is *more* in this case. A complete spectral and magnetic (including pmr[12]) characterization of the thermodynamics of such equilibria as shown by **1** and related chelates is in progress.

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[12] The chelates show isotropic proton contact shifts alternating in sign in the aromatic ring.

[13] To whom all correspondence should be addressed.

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Bis(cyclooctatetraenyl)uranium (Uranocene). A New Class of Sandwich Complexes That Utilize Atomic f Orbitals

Sir:

In a study of potential examples of hitherto unexplored[1] sandwich-type complexes between ten-electron π systems and suitable rare earth f orbitals, we have found an apparent example from the reaction of U^{4+} with cyclooctatetraene dianion. To the intense yellow solution prepared by allowing cyclooctatetraene (COT) to react with potassium in dry oxygen-free tetrahydrofuran (THF) at −30° is added a solution of uranium tetrachloride in THF at 0°. After stirring overnight, degassed water is added and the green crystals are filtered, extracted with benzene or toluene using an extraction thimble, and filtered again after cooling.[2] The minute green plates enflame on exposure to air but are stable to water, acetic acid, and aqueous sodium hydroxide. The compound is sparingly soluble in organic solvents and has a visible absorption spectrum with a cascade of bands at 616 (strong), 643, 661, and 671 (weak) mμ. It is thermally stable and sublimes at 180° (0.03 mm).

The structural assignment as bis(cyclooctatetraenyl)-uranium or "uranocene" comes primarily from the mass spectrum which has high intensity peaks at *m/e* 446 (molecular ion, $(C_8H_8)_2U^+ \equiv M$), 342 ($M - COT$), and 104 (COT) and a series of lower intensity peaks attributable to the cations of $M - C_6H_6$ (368), $U + C_6H_6$ (316), U (238), M/2 (223), and C_7H_7 (91). This mass spectrum is completely consistent with an assigned sandwich-complex structure of the ferrocene type with planar eight-membered rings above and below a central uranium atom in a D_{8d} or D_{8h} arrangement.

Although we plan to discuss the bonding of uranocene in more detail on completion of current studies of chemical and physical (X-ray structure, magnetic susceptibility, etc.) properties, the kinds of bonds possible may be mentioned here for the D_{8h} structure taken as an example. In this structure the 20 π electrons of the two COT^{2-} rings can be shared with vacant uranium orbitals in the symmetry-permitted combinations: $A_{1g} \rightarrow 7s$ ($+d_{z^2}$ which is probably weak); $A_{2u} \rightarrow 7p_z + 5f_{z^3}$ (probably weak); $E_{1g} \rightarrow 6d_{xz}$, $6d_{yz}$; $E_{1u} \rightarrow 5f_{xz^2} + 7p_x$, $5f_{yz^2} + 7p_y$; $E_{2g} \rightarrow d_{x^2-y^2}$, d_{xy}; $E_{2u} \rightarrow f_{xyz}$, $f_{z(x^2-y^2)}$.[3,4] It is this last combination that provides the most unique bonding feature of the present structure. Finally, the two electrons originally associated with U^{4+} can be placed in the degenerate back-bonding combination, $E_{3u} \leftarrow f_{x(x^2-3y^2)}$, $f_{y(3x^2-y^2)}$, and predicts a paramagnetic species. Similar combinations can be constructed for D_{8d}. These concepts imply that other ten-electron π systems should be potential ligands; such systems are currently being studied with several rare earth elements.

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[1] An examination of the literature has shown no mention of this type of bonding. The closest example we could find is the C_{8v} half-sandwich complex of a single planar cyclooctatetraene dianion with a central metal [M. A. Bennett, *Advan. Organomet. Chem.*, **4**, 376 (1966)]; the possible involvement of f orbitals in such complexes has, to our knowledge, not previously been discussed in the literature although the involvement of f orbitals has been proposed by W. Moffitt in the red compound, $(\pi\text{-}C_5H_5)_3UCl$ [L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 246 (1956)]. A red compound, $Ti(C_8H_8)_2$, and yellow $Ti_2(C_8H_8)_3$ have been reported [H. Breil and G. Wilke, *Angew. Chem. Intern. Ed. Engl.*, **5**, 898 (1966)]. The latter compound contains two planar eight-membered rings by X-ray determination [H. Dietrich and H. Dierks, *ibid.*, **5**, 899 (1966)] but both compounds are hydrolytically unstable and show the chemical behavior of highly ionic bonds to COT dianions.

[2] Repeat experiments have given yields up to 80% (G. Sonnichsen).

[3] For the symbolism of f orbitals, *cf.* H. G. Friedman, Jr., G. R. Choppin, and D. G. Feuerbacher, *J. Chem. Educ.*, 41, 354 (1964); C. Becker, *ibid.*, 41, 358 (1964).

[4] We are indebted to Dr. G. Sonnichsen for assistance in constructing these combinations.

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Direct Observation of Methyl-Substituted 7-Norbornadienyl and Bicyclo[3.2.0]heptadienyl Cations[1]

Sir:

An interesting facet of the chemistry of nonclassical carbonium ions deals with the rearrangements they can undergo.[2a] In this connection norbornadienyl cations have proved to be very instructive.[2b,c] Two monomethyl-substituted norbornadienyl cations, the 7-methyl ion I and the 2-methyl isomer II, and the rearrangement of I to II were reported recently.[2c] We now report direct observation of the two remaining monomethylnorbornadienyl cations, the 1-methyl species III and the 5-methyl isomer IV, as well as the rearrangement of III to IV. The new data elucidate further the quantitative relationships between the bicyclo[2.2.1]heptadienyl cations and their bicyclo-[3.2.0] isomers.[2b]

For the successful generation of the 1- and 5-methyl-7-norbornadienyl cations III and IV we made use of the ring-expanding isomerization of the 2-methylbicyclo[3.2.0]heptadienyl cation VI to its bicyclo-

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[1] Research supported by the National Science Foundation.

[2] (a) S. Winstein, *Experientia Suppl.*, 137 (1955); L. de Vries and S. Winstein, *J. Am. Chem. Soc.*, **82**, 5363 (1960); (b) R. K. Lustgarten, M. Brookhart, and S. Winstein, *ibid.*, **89**, 6350 (1967); (c) M. Brookhart and R. K. Lustgarten, *ibid.*, **89**, 6352 (1967).